IR-9 Coordination Compounds (Draft March 2004)

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IR-9.1 INTRODUCTION

IR-9.1.1 General

This Chapter presents the definitions and rules necessary for formulating and naming coordination compounds. Key terms such as coordination entity, coordination polyhedron, coordination number, chelation and bridging ligands are first defined and the role of additive nomenclature explained (see also Chapter IR-7).

These definitions are then used to develop rules for writing the names and formulae of coordination compounds. The rules allow the composition of coordination compounds to be described in a way that is as unambiguous as possible. The names and formulae provide information about the nature of the central atom, the ligands that are attached to it, and the overall charge on the structure.

Stereochemical descriptors are then introduced as a means of identifying or distinguishing between the diastereoisomeric or enantiomeric structures that may exist for a compound of any particular composition.

The description of the configuration of a coordination compound requires first that the coordination geometry be specified using a polyhedral symbol (Section IR-9.3.2.1). Once this is done the relative positions of the ligands around the coordination polyhedron are specified using the configuration index (Section IR-9.3.3). The configuration index is a sequence of ligand priority numbers produced by following rules specific to each coordination geometry. If required, the chirality of a coordination compound can be described, again using ligand priority numbers (Section IR-9.3.4). The ligand priority numbers used in these descriptions are based on the chemical composition of the ligands. A detailed description of the rules by which they are obtained is provided in Section P-91 of Ref. 1, but an outline is given in Section IR-9.3.5.

IR-9.1.2 Definitions

IR-9.1.2.1 *Background*

The development of coordination theory and the identification of a class of compounds called coordination compounds began with the historically significant concepts of primary and secondary valence.

Primary valences were obvious from the stoichiometries of simple compounds such as $NiCl_2$, $Fe_2(SO_4)_3$, and $PtCl_2$. However, new materials were frequently observed when other, independently stable substances, *e.g.* H_2O, NH_3, and KCl, were added to these simple compounds giving, for example, $NiCl_2{\cdot}4H_2O$, $Co_2(SO_4)_3{\cdot}12NH_3$ or $PtCl_2{\cdot}2KCl$. Such species were called complex compounds, in recognition of the stoichiometric complications they represented, and were considered characteristic of certain metallic elements. The number of species considered to be added to the simple compounds gave rise to the concept of secondary valence.

Recognition of the relationships between these complex compounds led to the formulation of coordination theory and the naming of coordination compounds using additive nomenclature. Each coordination compound either is, or contains, a coordination entity (or complex) that consists of a central atom to which other groups are bound.

While these concepts have usually been applied to metal compounds, a wide range of other species can be considered to consist of a central atom to which a number of other groups are bound. The application of additive nomenclature to such species is described in Chapter 7.

IR-9.1.2.2 *Coordination compounds and the coordination entity*

A coordination compound is any compound that contains a coordination entity. A coordination entity is an ion or neutral molecule that is composed of a central atom, usually that of a metal, to which is attached a surrounding array of other atoms or groups of atoms, each of which is called a ligand. Classically, a ligand was said to satisfy either a secondary or a primary valence of the central atom and the sum of these valences (often equal to the number of ligands) was called the coordination number (see Section I-9.1.2.6). In formulae, the coordination entity is enclosed in square brackets whether it is charged or uncharged (see Section I-9.2.3.2).

Examples:

1. $[Co(NH_3)_6]^{3+}$
2. $[PtCl_4]^{2-}$
3. $[Fe_3(CO)_{12}]$

IR-9.1.2.3 *Central atom*

The central atom is the atom in a coordination entity which binds other atoms or groups of atoms (ligands) to itself, thereby occupying a central position in the coordination entity. The central atoms in $[NiCl_2(H_2O)_4]$, $[Co(NH_3)_6]^{3+}$ and $[PtCl_4]^{2-}$ are nickel, cobalt and platinum, respectively.

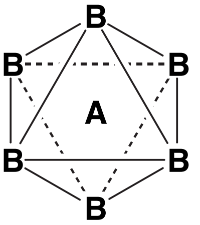
IR-9.1.2.4 *Ligands*

The ligands are the atoms or groups of atoms bound to the central atom. The root of the word is often converted into other forms, such as to ligate, meaning to coordinate as a ligand, and the derived participles, ligating and ligated.

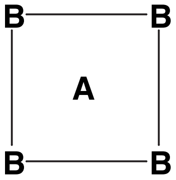
IR-9.1.2.5 *Coordination polyhedron*

It is standard practice to regard the ligand atoms directly attached to the central atom as defining a coordination polyhedron (or polygon) about the central atom. Thus $[Co(NH_3)_6]^{3+}$ is an octahedral ion and $[PtCl_4]^{2-}$ is a square planar ion. In this way the coordination number may equal the number of vertices in the coordination polyhedron. This definition does not necessarily apply to organometallic compounds, where more than one atom of the ligand may be involved in a single bond to the central atom (see Chapter IR-10).

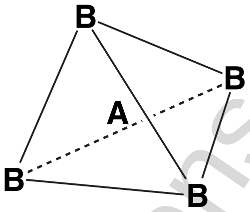
Examples:



1. octahedral coordination polyhedron



2. square planar coordination polygon



3. tetrahedral coordination polyhedron

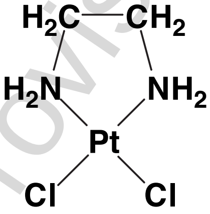
IR-9.1.2.6 *Coordination number*

For coordination compounds, the coordination number equals the number of σ-bonds between ligands and the central atom. Note that where both σ- and π-bonding occurs between the ligating atom and the central atom, *e.g.* with ligands such as CN^-, CO, N_2 and PMe_3, the π-bonds are not considered in determining the coordination number.

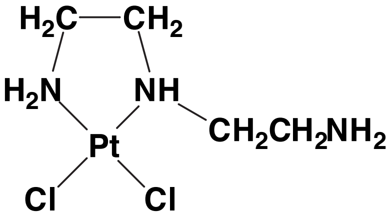
IR-9.1.2.7 *Chelation*

Chelation involves coordination of more than one σ-electron pair donor atom from the same ligand to the same central atom. The number of such ligating atoms in a single chelating ligand is indicated by the adjectives bidentate,[2] tridentate, tetradentate, pentadentate, *etc*. (see Table IV* for a list of numerical prefixes). The number of donor atoms from a given ligand attached to the same central atom is called the denticity.

Examples:



1. bidentate chelation



2. bidentate chelation

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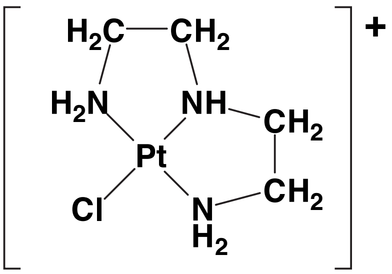
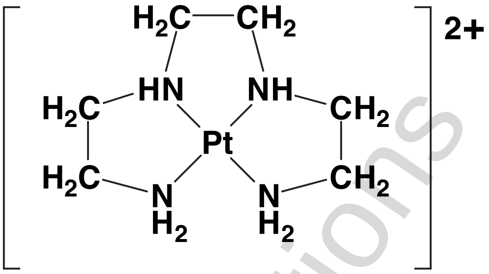
* Tables numbered with a Roman numeral are collected together at the end of this book.



3. tridentate chelation



4. tetradentate chelation

The cyclic structures formed when more than one donor atom from the same ligand is bound to the central atom are called chelate rings, and the process of coordination of these donor atoms is called chelation.

If a potentially bidentate ligand, such as ethane-1,2-diamine, coordinates to two metal ions, it does NOT chelate but coordinates in a monodentate fashion to each metal ion, forming a connecting link or bridge.

Example:

1. $[(H_3N)_5Co(\mu\text{-}NH_2CH_2CH_2NH_2)Co(NH_3)_5]^{6+}$

Alkenes, arenes and other unsaturated molecules attach to central atoms, using some or all of their multiply bonded atoms, to give organometallic complexes. While there are many similarities between the nomenclature of coordination and organometallic compounds, the latter differ from the former in clearly definable ways. Organometallic complexes are therefore treated separately in Chapter IR-10.

IR-9.1.2.8 *Oxidation state*

The oxidation state of a central atom in a coordination entity is defined as the charge it would bear if all the ligands were removed along with the electron pairs that were shared with the central atom. It is represented by a Roman numeral.

The general and systematic treatment of oxidation state follows from the application of the classical definition of coordination number. It must be emphasized that oxidation state is an index derived from a simple and formal set of rules (see also Sections IR-4.6.1 and IR-5.4.2.2) and that it is not a direct indicator of electron distribution. In certain cases, the formalism does not give acceptable central atom oxidation states. In such ambiguous cases, the net charge on the coordination entity is preferred in most nomenclature practices. The following examples illustrate the relationship between oxidation state and coordination number.

	Formula	*Ligands*	*Central atom oxidation state*
1.	$[Co(NH_3)_6]^{3+}$	6 NH_3	III
2.	$[CoCl_4]^{2-}$	4 Cl^-	II
3.	$[MnO_4]^-$	4 O^{2-}	VII
4.	$[MnFO_3]$	3 O^{2-} + 1 F^-	VII
5.	$[Co(CN)_5H]^{3-}$	5 CN^- + 1 H^-	III
6.	$[Fe(CO)_4]^{2-}$	4 CO	-II

IR-9.1.2.9 *Coordination nomenclature: an additive nomenclature*

When coordination theory was first developed, coordination compounds were considered to be formed by addition of independently stable compounds to a simple central compound. They were therefore named on the basis of an additive principle, where the names of the added compounds and the central simple compound were combined. This principle remains the basis for naming coordination compounds.

The name is built up around the central atom name, just as the coordination entity is built up around the central atom.

Example:

1. Addition of ligands to a central atom:

$$Ni^{2+} + 6H_2O \longrightarrow [Ni(OH_2)_6]^{2+}$$

Addition of ligand names to a central atom name:

hexaaquanickel(II)

This nomenclature then extends to more complicated structures where central atoms (and their ligands) are added together to form polynuclear species from mononuclear building blocks.

IR-9.1.2.10 *Bridging ligands*

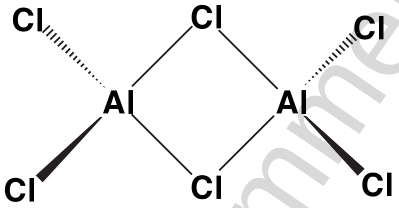
In polynuclear species a ligand can also act as a bridging group, by forming bonds to two or more central atoms simultaneously. Bridging is indicated in names and formulae by adding the symbol μ as a prefix to the ligand formula or name (see Section IR-9.2.5.2).

Bridging ligands link central atoms together to produce coordination entities having more than one central atom. The number of central atoms joined into a single coordination entity by bridging ligands or metal-metal bonds is indicated by using the terms dinuclear, trinuclear, tetranuclear, *etc*.

The bridge index is the number of central atoms linked by a particular bridging ligand (see Section IR-9.2.5.2). Bridging can be through one atom or through a longer array of atoms.

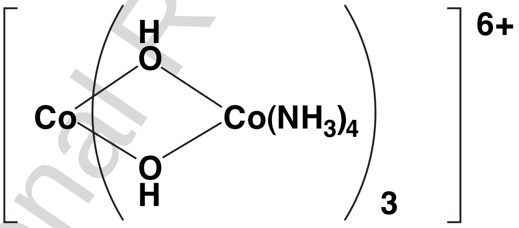
Examples:

1.



$Al_2(\mu\text{-}Cl)_2Cl_4$ or $Cl_2Al(\mu\text{-}Cl)_2AlCl_2$

2.



$[Co\{(\mu\text{-}OH)_2Co(NH_3)_4\}_3]^{6+}$

IR-9.1.2.11 *Metal-metal bonds*

Simple structures that contain a metal-metal bond are readily described using additive nomenclature (see Section IR-9.2.5.3), but complications arise for structures that involve three or more central atoms. Species that contain such clusters of central atoms are treated in Sections IR-9.2.5.6 to IR-9.2.5.8.

Examples:

1. $[Br_4ReReBr_4]^{2+}$
   bis(tetrabromidorhenium)(*Re*—*Re*)

2.

1 2

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

IR-9.2 DESCRIBING THE CONSTITUTION OF COORDINATION COMPOUNDS

IR-9.2.1 General

Three main methods are available for describing the constitution of compounds; one can draw structures, write names or write formulae. A drawn structure contains information about the structural components of the molecule as well as their stereochemical relationships. Unfortunately, such structures are not usually suitable for inclusion in text. Names and formulae are therefore used to describe the chemical composition of a compound.

The name of a coordination compound provides detailed information about the structural components present. However, it is important that the name can be easily interpreted unambiguously. For that reason, there should be rules that define how the name is constructed. The following sections detail these rules and provide examples of their use.

The name of a compound can, however, be rather long and its use may be inconvenient. In such circumstances a formula provides a shorthand method of representing the compound. Rules are provided in order to make the use of formulae more straightforward. It should be noted that, because of their abbreviated form, it is often not possible to provide as much information about the structure of a compound in its formula as can be provided by its name.

IR-9.2.2 Naming coordination compounds

The names of coordination compounds are derived by following the principles of additive nomenclature, as outlined in Chapter IR-7. Thus, the groups that surround the central atom or structure must be identified in the name. They are listed as prefixes to the name of the central atom (see Section IR-9.2.2.1) along with any appropriate multipliers (see Section IR-9.2.2.2). These prefixes are usually derived in a simple way from the ligand name (see Section IR-9.2.2.3).

IR-9.2.2.1 *Sequences of ligands and central atoms within names*

The following rules are used when naming coordination compounds:

(i) ligand names are listed before the name of the central atom,
(ii) no spaces are left between parts of the name that refer to the same coordination entity,

(iii) ligand names are listed in alphabetical order (numerical prefixes indicating the number of ligands are not considered in determining that order),

(iv) the use of abbreviations in *names* is discouraged.

Example:

1. $[CoCl(NH_3)_5]Cl_2$
penta*a*mmine*c*hloridocobalt(2+) chloride

2. $[AuXe_4]^{2+}$
tetraxenonidogold(2+)

IR-9.2.2.2 *Number of ligands in a coordination entity*

Two kinds of numerical prefix are available for indicating the number of each type of ligand within the name of the coordination entity (see Table IV).

(i) Prefixes di, tri, *etc*. are generally used for simple ligands. Enclosing marks are not required.

(ii) Prefixes bis, tris, tetrakis, *etc*. are used with complex expressions and when required to avoid ambiguity. Enclosing marks (the nesting order of which is described in Section IR-2.2) must be placed around the multiplicand.

For example, one would use diammine, for $(NH_3)_2$, but bis(methylamine), for $(NH_2Me)_2$, to make a distinction from dimethylamine. (Note that this ambiguity does not arise if the preferred IUPAC name[1], methanamine, is used instead of methylamine). There is no elision of vowels or use of a hyphen, *e.g*. in tetraammine and similar names.

IR-9.2.2.3 *Representing ligands in names*

Systematic and alternative names for some common ligands are given in Table IX. The general features are as follows:

(i) Names of anionic ligands, whether inorganic or organic, are modified to end in 'o' (see Section IR-7.1.3). 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. In particular, alcoholates, thiolates, phenolates, carboxylates, partially dehydronated amines, phosphanes, *etc*. are in this category.[3]

In its complexes, hydrogen is always treated as anionic**.** 'Hydrido' is used for hydrogen coordinating to all elements including boron.[4]

(ii) Names of neutral and cationic ligand names, including organic ligands,[5] are used without modification (even if they carry the endings 'ide', 'ite' or 'ate').

(iii) Enclosing marks are required for neutral and cationic ligand names, for inorganic anionic ligands containing numerical prefixes (such as triphosphato), for any compositional name (such as carbon disulfide), for any substituted organic ligand (even if there is no ambiguity in its use), and wherever necessary to avoid ambiguity. However, common ligands such as aqua, ammine, carbonyl, nitrosyl, methyl, ethyl, *etc*., do not require enclosing marks, unless there is ambiguity.

(iv) Ligands binding to metals through carbon atoms are treated in Chapter IR-10, on organometallic compounds.

Examples:

	Formula	*Ligand name*
1.	Cl^-	chlorido[3]
2.	CN^-	cyanido[3]
3.	H^-	hydrido
4.	D^- or $^2H^-$	deuterido or [^{2}H]hydrido
5.	$PhCH_2CH_2Se^-$	2-phenylethaneselanolato
6.	$MeCOO^-$	acetato or ethanoato
7.	Me_2N^-	dimethylazanido or dimethylamido
8.	$MeCONH_2$	acetamide (not acetamido)
9.	$MeCONH^-$	acetylazanido or acetylamido (not acetamido)
10.	$MeNH_2$	methanamine
11.	$MeNH^-$	methylazanido or methanaminido (anion itself named methanaminide, see Section P-72.2.2.3 of Ref. 1)
12.	$MePH_2$	methylphosphane
13.	$MePH^-$	methylphosphanido
14.	$MeOS(O)OH$	methyl hydrogen sulfite
15.	$MeOS(O)O^-$	methyl sulfito, or methoxidodioxidosulfato(1-)

IR-9.2.2.4 *Charge numbers, oxidation numbers, and ionic proportions*

The following methods can be used to assist in describing the composition of a compound:

(i) All anionic coordination entities take the ending 'ate', whereas no distinguishing termination is used for cationic or neutral coordination entities.

(ii) The oxidation number of the central atom may be indicated by appending a Roman numeral to the central atom name, but only if the oxidation state can be defined without ambiguity. The oxidation number is enclosed in parentheses after the part of the name denoting the central atom. When necessary a negative sign is placed before the number. Arabic zero indicates the zero oxidation number.

(iii) Alternatively, the charge on a coordination entity may be indicated. The net charge is written in arabic numbers, with the number preceding the charge sign, and enclosed in parentheses. It follows the name of the central atom without the intervention of a space.

(iv) The proportions of ionic entities may be given by using stoichiometric prefixes on both ions.

Examples:

1. $K_4[Fe(CN)_6]$
   potassium hexacyanidoferrate(II), or
   potassium hexacyanidoferrate(4−), or
   tetrapotassium hexacyanidoferrate
2. $[Co(NH_3)_6]Cl_3$
   hexaamminecobalt(III) chloride
3. $[CoCl(NH_3)_5]Cl_2$
   pentaamminechloridocobalt(2+) chloride
4. $[CoCl(NH_3)_4(NO_2)]Cl$
   tetraamminechloridonitrito-κ*N*-cobalt(III) chloride
5. $[PtCl(NH_2Me)(NH_3)_2]Cl$
   diamminechlorido(methanamine)platinum(II) chloride
6. $[CuCl_2\{O{=}C(NH_2)_2\}_2]$
   dichloridobis(urea)copper(II)
7. $K_2[PdCl_4]$
   potassium tetrachloridopalladate(II)
8. $K_2[OsCl_5N]$
   potassium pentachloridonitridoosmate(2−)
9. $Na[PtBrCl(NH_3)(NO_2)]$
   sodium amminebromidochloridonitrito-κ*N*-platinate(1−)
10. $[Fe(CNMe)_6]Br_2$
    hexakis(methyl isocyanide)iron(II) bromide
11. $[Co(en)_3]Cl_3$
    tris(ethane-1,2-diamine)cobalt(III) trichloride

IR-9.2.3 Formulae of coordination compounds

The formula of a compound is a shorthand tool used to provide basic information about the constitution of the compound in a concise and convenient manner. Different applications may require flexibility in the writing of formulae. Thus, on occasion, it may be desirable to violate the following guidelines in order to provide more information about the structure of the compound that the formula represents.

IR-9.2.3.1 *Sequence of symbols within the coordination formula*

(i) The central atom is listed first.

(ii) The ligands are then listed in alphabetical order[6] (see Section IR-4.4.2.2), based on the way the ligand is represented in the formula. Thus, CH_3CN, MeCN and NCMe would be ordered under C, M and N respectively. The placement of the ligand in the list does not depend on the charge of the ligand. Polydentate ligands are included in the alphabetical list, according to Section IR-4.4.2.2. If an abbreviation is used in a formula to represent a ligand (see Section IR-9.2.3.4), the first letter of the abbreviation is used to determine the position of the ligand in the alphabetical list.

(iii) More information is conveyed by formulae that show ligands with the donor atom nearest the central atom; this procedure is recommended wherever possible, even for coordinated water.

(iv) Ligand linear formulae are sometimes needed.

IR-9.2.3.2 *Use of enclosing marks*

The formula for the entire coordination entity, whether charged or not, is enclosed in square brackets. When ligands are polyatomic, their formulae are enclosed in parentheses. Ligand abbreviations are also usually enclosed in parentheses. In the special case of coordination entities, the nesting order of enclosures is as given in Sections IR-2.2 and IR-4.2.3. Square brackets are used only to enclose coordination entities, and parentheses and braces are nested alternately. There should be no space between representations of ionic species within a coordination formula.

Examples 1-11 in Section IR-9.2.2.4 also illustrate the use of enclosing marks in formulae.

IR-9.2.3.3 *Ionic charges and oxidation numbers*

If the formula of a charged coordination entity is to be written without that of the counter-ion, the charge is indicated outside the square bracket as a right superscript, with the number before the sign. The oxidation number of a central atom may be represented by a Roman numeral, which should be placed as a right superscript on the element symbol.

Examples:

1. $[PtCl_6]^{2-}$
2. $[Cr(OH_2)_6]^{3+}$
3. $[Cr^{III}(NCS)_4(NH_3)_2]^{-}$
4. $[Cr^{III}Cl_3(OH_2)_3]$
5. $[Fe^{-II}(CO)_4]^{2-}$

IR-9.2.3.4 *Use of abbreviations*

Abbreviations can be used to represent complicated organic ligands in formulae (although they should not normally be used in names). When used in formulae they are usually enclosed in parentheses.

Guidelines for the formulation of ligand abbreviations are given in Section IR-4.4.4; examples of such abbreviations are listed alphabetically in Table VII with diagrams of most shown in Table VIII.

In cases where coordination occurs through one donor atom of a ligand containing more than one possible donor site, an indication of that donor atom may be desirable. This may be achieved through use of the kappa convention (see Section IR-9.2.4.2) in which the Greek lower case kappa (κ) is used to indicate the donor atom. For example, if the glycinate anion (gly) coordinates only through the nitrogen, the abbreviation of the ligand would be shown as gly-κ*N*, as in the complex $[M(\text{gly-}\kappa N)_3X_3]$.

IR-9.2.4 Specifying donor atoms

IR-9.2.4.1 *General*

There is no need to specify the donor atom of a monodentate ligand that has only one atom able to form a bond with a central atom. However, ambiguity may arise when there is more than one possible donor atom in a ligand. It is then necessary to specify which donor atom(s) of a ligand is (are) bound to the central atom. In particular, this must be done in any case where there are potential donor atoms that are not bound to the central atom or if there is more than one central atom. The only exceptions are common ligands that typically coordinate in a manner that leaves a potential donor atom uncoordinated. Thus, in terms of nomenclature, carboxylate groups are usually considered to be monodentate unless otherwise specified, and carbonyl and nitrosyl ligands are presumed to bind in a monodentate fashion, through the carbon and nitrogen atoms respectively.

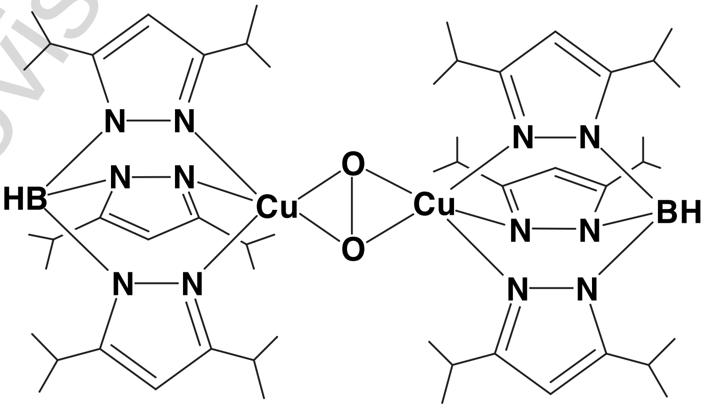
In general, however, ligands are presumed to coordinate through all of their donor atoms, unless otherwise specified. The following sections detail the means by which donor atoms are specified in those systems where not all donor atoms are coordinated. The first method, the kappa (κ) convention, is general and can be used for systems of great complexity. The second, use of the donor atom symbol, is appropriate only for relatively simple systems.

These systems may be used in names, but they are not always suitable for use in formulae. The use of donor atom symbols is possible in the formulae of simple systems, but care must be taken to avoid ambiguity. The kappa convention is not generally compatible with the use of abbreviations.

It should be noted that these methods are only appropriate for cases where each bond is between the central atom and a single donor atom. The eta (η) nomenclature should be used for any cases where the central atom is bonded to contiguous donor atoms (see IR-10.2.5.1). Most examples of this latter kind are organometallic compounds (Chapter IR-10) but the example below shows its use for a coordination compound of dioxygen.

Example:

1.



μ-η^2:η^2-bonding of dioxygen

IR-9.2.4.2 *The kappa convention*

The kappa convention is used to indicate the points of ligation, particularly in complex examples. Single ligating atom attachments of a polyatomic ligand to a coordination centre are indicated by the italicized element symbol preceded by a Greek kappa, κ. These symbols are placed after the portion of the ligand name that represents the ring, chain or substituent group in which the ligating atom is found.

Monodentate ambidentate ligands provide simple examples, although for these cases the kappa convention is not significantly more useful than the 'donor atom symbol' convention (Section IR-9.2.4.4). Nitrogen-bonded NCS is thiocyanato-κ*N* and sulfur-bonded NCS is thiocyanato-κ*S*. Nitrogen-bonded nitrite is named nitrito-κ*N* and oxygen-bonded nitrite is named nitrito-κ*O* as in pentaamminenitrito-κ*O*-cobalt(III).

In cases where two or more identical ligands (or parts of a polydentate ligand) are involved, a superscript is used on κ.

Example:

1. $[NiBr_2(Me_2PCH_2CH_2PMe_2)]$
dibromido[ethane-1,2-diylbis(dimethylphosphane)-κ^2P]nickel(II)

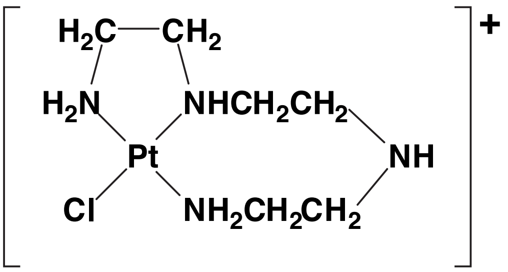
Donor atoms of a particular element may be distinguished by adding a prime or primes, or a right superscript numeral, to the element symbol. Primes may be sufficient in simple cases. (See Example 3 below).

Superscript numerals, on the other hand, are based on an appropriate numbering of some or all of the atoms of the ligand and allow the position of the bond(s) to the central atom to be specified even in quite complex cases. (See Example 4 below).

Any multiplicative prefixes for complex entities are presumed to operate on the κ symbol as well. Thus, one uses the partial name '...bis(2-amino-κ*N*-ethyl)... ' and not '...bis(2-amino-κ^2N-ethyl)...' in Example 2 below. Examples 2 and 3 use tridentate chelation by the linear tetraamine ligand *N*,*N*'-bis(2-aminoethyl)ethane-1,2-diamine to illustrate these rules.

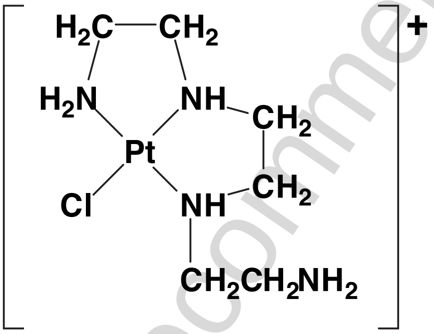
Examples:

2.



[*N*,*N*'-bis(2-amino-κ*N*-ethyl)ethane-1,2-diamine-κ*N*]chloridoplatinum(II)

3.



[*N*-(2-amino-κ*N*-ethyl)-*N*'-(2-aminoethyl)ethane-1,2-diamine-κ^2*N*,*N*']chloridoplatinum(II)

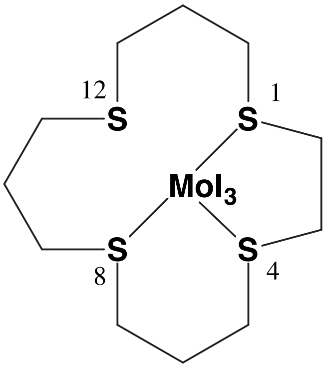
Example 2 illustrates how coordination by the two terminal primary amino groups of the ligand is indicated by placing the kappa index after the functional group name and within the effect of the 'bis' doubling prefix. The appearance of the simple index κ*N* after the 'ethane-1,2-diamine' indicates the binding by only one of the two equivalent secondary amino nitrogen atoms.

Only one of the primary amines is coordinated in Example 3. This is indicated by not using the doubling prefix 'bis', repeating (2-aminoethyl), and inserting the κ index only in the first such unit, *i.e*. (2-amino-κ*N*-ethyl). The involvement of both of the secondary ethane-1,2-diamine nitrogen atoms in chelation is indicated by the index κ^2*N*,*N*'.

Tridentate chelation by the tetrafunctional macrocycle in Example 4 is shown by the kappa index following the ligand name. The ligand locants are required in order to distinguish this complex from those where the central atom is bound to other combinations of the four potential donor atoms.

Example:

4.

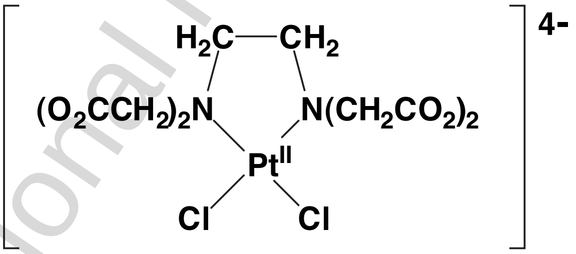


triiodido(1,4,8,12-tetrathiacyclopentadecane-κ^3*S*^{1,4,8})molybdenum, or
triiodido(1,4,8,12-tetrathiacyclopentadecane-κ^3*S*^{1},*S*^{4},*S*^{8})molybdenum

Well established modes of chelation of the (ethane-1,2-diyldinitrilo)tetraacetato ligand (edta), namely bidentate, tetradentate and pentadentate, are illustrated in Examples 5-8. The multiplicative prefix 'tetra' used in Example 5 cannot be used in Examples 6 and 7 because of the need to avoid ambiguity about which acetate arms are coordinated to the central atom.

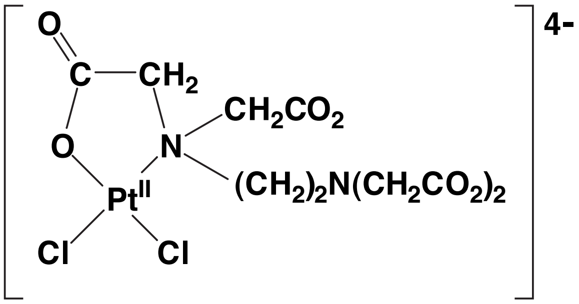
Examples:

5.



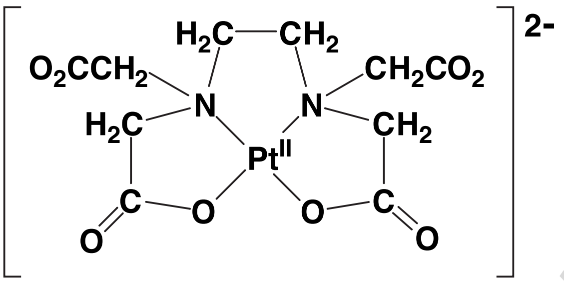
dichlorido[(ethane-1,2-diyldinitrilo-κ^2*N*,*N*')tetraacetato]platinate(4−)

6.



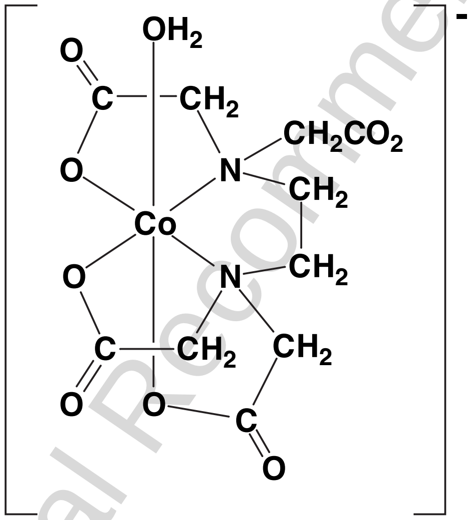
dichlorido[(ethane-1,2-diyldinitrilo-κ*N*)(*N*-acetato-κ*O*)triacetato]platinate(II)

7.



[(ethane-1,2-diyldinitrilo-κ^2N,N')(N,N'-diacetato-κ^2O,O')-N,N-diacetato]platinate(2−)

8.



aqua[(ethane-1,2-diyldinitrilo-κ^2N,N')tetraacetato-κ^3O,O',O'']cobaltate(1−)

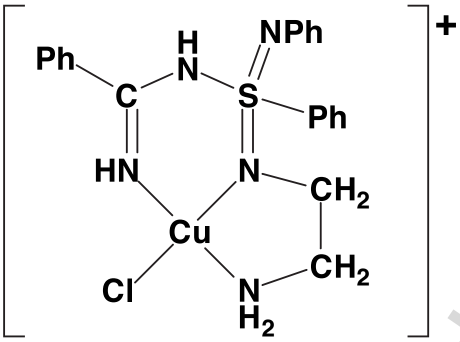
A compound of edta in which one amino group is not coordinated while all four acetates are bound to a single metal ion would bear the ligand name (ethane-1,2-diyldinitrilo-κN)tetraacetato-κ^4O,O',O'',O''' within the name of the complex.

The mixed sulfur-oxygen cyclic polyether 1,7,13-trioxa-4,10,16-trithiacyclooctadecane might chelate to alkali metals only through its oxygen atoms and to second row transition atoms only through its sulfur atoms. The corresponding kappa indexes for such chelate complexes would be κ^3O^1,O^7,O^{13} and $\kappa^3S^4,S^{10},S^{16}$, respectively.

Examples 9, 10 and 11 illustrate three modes of chelation of the ligand *N*-[*N*-(2-aminoethyl)-*N'*,*S*-diphenylsulfonodiimidoyl]benzamidine. The use of kappa indexes allows these binding modes (and others) to be distinguished and identified, in spite of the abundance of heteroatoms that could coordinate.

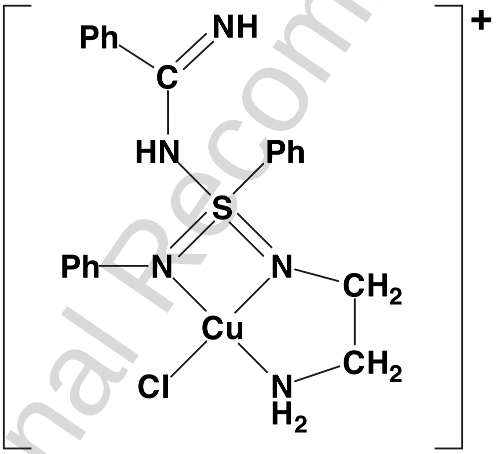
Examples:

9.



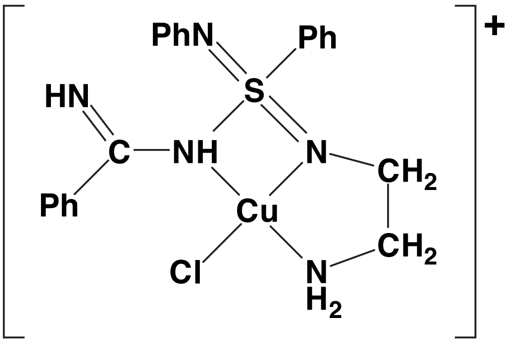
{*N*-[*N*-2-(amino-κ*N*-ethyl)-*N*'-phenylbenzenesulfonodiimidoyl-κ*N*]benzenimidamide-κ*N*'}chloridocopper(II)

10.



{*N*-[*N*-2-(amino-κ*N*-ethyl)-*N*'-phenylbenzenesulfonodiimidoyl-κ^2*N*,*N*']benzenimidamide}chloridocopper(II)

11.



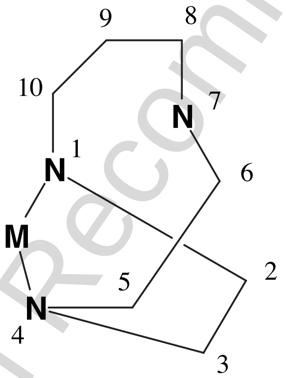
{*N*-[*N*-2-(amino-κ*N*-ethyl)-*N*'-phenylbenzenesulfonodiimidoyl-κ*N*]benzenimidamide-κ*N*'}chloridocopper(II)

The distinction between the names in Examples 9 and 11 rests on the conventional priming of the second nitrogen atom in the benzenimidamide functional group. The prime identifies the imino benzenimidamide nitrogen atom, which is more remote from the 2-aminoethyl group (where the name began).

The use of donor atom locants on the atomic symbols to indicate point-of-ligation is illustrated by the two isomeric bidentate modes of binding of the macrocycle 1,4,7-triazacyclodecane (Examples 12 and 13). Conveying the formation of the five-membered chelate ring requires the index $\kappa^{2}\mathit{N}^{1},\mathit{N}^{4}$, while the six-membered chelate ring requires the index $\kappa^{2}\mathit{N}^{1},\mathit{N}^{7}$. The naming of a complex structure is shown in Example 14.

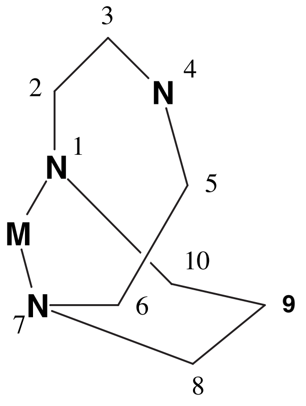
Examples:

12.



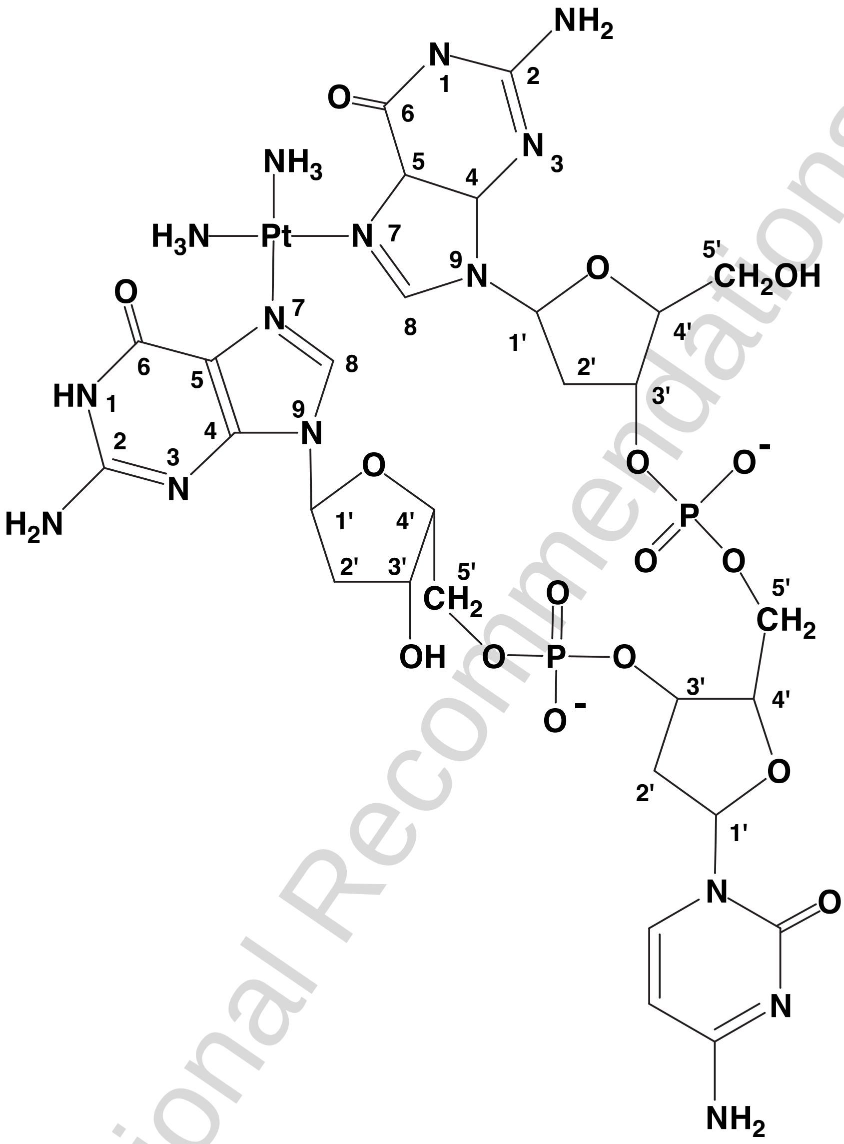
$\kappa^{2}\mathit{N}^{1},\mathit{N}^{4}$

13.



$\kappa^{2}\mathit{N}^{1},\mathit{N}^{7}$.

14.



diammine[2'-deoxyguanylyl-κN^7-(3' → 5')-2'-deoxycytidylyl(3' → 5')-2'-deoxyguanosinato(2−)-κN^7]platinum(II)

IR-9.2.4.3 *Comparison of the eta and kappa nomenclatures*

The modifiers eta, η, and kappa, κ, are complementary and should not be interchanged in usage. The eta nomenclature (Section IR-10.2.5.1) is used to specify the number of contiguous donor atoms involved in the bond to a central atom (hapticity). It is required only when there is more than one ligand atom involved in the bond to the central atom (*i.e.* the term η^1 is not required). The contiguous atoms are often the same element, but need not be.

The kappa nomenclature is used to specify the point of attachment to the metal in the event a ligand contains several different possible points of attachment (that are not all used), or to specify the point of attachment of the same ligand to different metal centres in a polynuclear complex.

In cases where two or more identical ligands (or parts of a polydentate ligand) are bound to a central atom, a superscript may be used on κ to indicate the number of donor atoms.

IR-9.2.4.4 *Donor atom symbol to indicate points of ligation*

Donor atoms of a ligand may be denoted by adding the italicized symbol(s) for the donor atom (or atoms) to the end of the name (or formula) of the ligand. Thus, the 1,2-dithiooxalate anion may conceivably be attached through S or O, and possible bidentate coordination modes are distinguished by indicating the donor atoms: 1,2-dithiooxalato-*S,S'*; 1,2-dithiooxalato-*O,O'*; 1,2-dithiooxalato-*O,S*; 1,2-dithiooxalato-*O,S'*. A similar approach may be used for ligands such as thiocyanate and nitrite. The following system of citation of ligating atoms is suggested for simple cases. (The kappa convention should be used for complicated cases).

For ligands with ligating atoms linearly arranged along a chain, the order of citation symbols should be successive, starting at one end. The choice of end is based upon alphabetical order if the ligating atoms are different, *e.g.* cysteinato-*N,S*; cysteinato-*N,O*. When no such simple distinction can be made, the ligating atom at the site with the lowest locant assigned according to organic practice (see Section P-14.3.4 of Ref. 1) is given preference.

Examples:

1. $(CF_3COCHCOMe)^-$

   1,1,1-trifluoro-2,4-dioxopentan-3-ido-*O* would be used to refer to coordination of the CF_3CO portion of the molecule, since it is preferred to (*i.e.* has a lower locant than) MeCO, which would be identified by *O'*.

2. $H_2NCH(Me)CH_2NH_2$

   propane-1,2-diamine-*N* would be used to refer to coordination of the NH_2CH_2 portion of the molecule, since it is preferred to (*i.e.* has a lower locant than) NH_2CHMe, which would be identified by *N'*.

If the same element is involved in the different positions, the place in the chain or ring to which the central atom is attached may alternatively be indicated by numerical superscripts. It may be necessary to provide numerical superscripts where none is available from normal organic substitutive nomenclature.

3. $(MeCOCHCOMe)^-$

2,4-dioxopentan-3-ido-*C*^{3} indicates coordination through the central carbon atom.

IR-9.2.5 Polynuclear complexes

IR-9.2.5.1 *General*

Polynuclear inorganic compounds exist in a bewildering array of structural types, such as ionic solids, molecular polymers, extended assemblies of oxoanions, chains and rings, bridged metal complexes, and homo- and hetero-nuclear clusters. This section primarily treats the nomenclature of bridged metal complexes and homo- and hetero-nuclear clusters. Coordination polymers are treated extensively elsewhere.[7]

As a general principle, as much structural information as possible should be presented when writing the name or formula of a polynuclear complex. However, polynuclear complexes may have structures so large and extended as to make a rational structure-based nomenclature impractical. Furthermore, their structures may be undefined or not suitably elucidated. In such cases, the principal function of the name or formula is to convey the stoichiometric proportions of the various moieties present.

Ligands are cited in the usual alphabetical order with appropriate numerical prefixes. The central atoms are listed using the atom priority derived from Table VI; the first reached on following the direction of the arrow is placed last. The central atoms are placed after the ligands when naming a complex and before the ligands in the formula of the complex.

The number of central atoms of a given kind, if greater than one, is indicated in names by a numerical prefix (Example 1). For anionic species, the suffix 'ate' and the number indicating the charge on the ion are added after the central atom list; the list of central atoms is then enclosed in parentheses (Example 2).

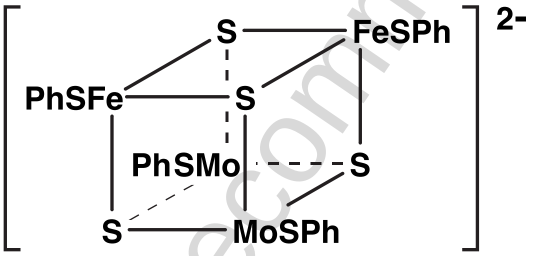
Where necessary, the symbol kappa, κ, with the italicized atomic symbol(s) of the donor(s) is employed to indicate the ligating atom(s) (Section IR-9.2.4.2). The distribution of ligands between the central atoms is indicated by including a number, to the left of each kappa symbol, which refers to the position of the central atom in the list at the end of the name. This number is the priority of the central atom derived from Table VI (Example 3). Thus the inclusion of (benzenethiolato-1κ*S*) in a name would indicate that the sulfur atom of benzenethiolate is bonded to central atom number 1.

These general rules may be relaxed in order to provide additional information, if available. For example, the order of symbols in a formula may be changed to reflect the structure of a molecule. In this case it is preferable to write the formula of the ligand so that the donor atom is placed close to the central atom to which it is attached. More details are given in the following sections.

Examples:

1. $[Rh_3H_3\{P(OMe)_3\}_6]$

   trihydridohexakis(trimethyl phosphite)trirhodium

2. 

   $[Mo_2Fe_2S_4(SPh)_4]^{2-}$

   tetrakis(benzenethiolato)-1κ*S*,2κ*S*,3κ*S*,4κ*S*-tetra-μ$_3$-sulfido-*tetrahedro*-(dimolybdenumdiiron)ate(2−)

3. $[(OC)_5\overset{1}{Re}\overset{2}{Co}(CO)_4]$

   nonacarbonyl-1κ^5*C*,2κ^4*C*-rheniumcobalt(*Re—Co*)

IR-9.2.5.2 *Bridging ligands*

Bridging ligands, as far as they can be specified, are indicated by the Greek letter μ appearing before the ligand name and separated from it by a hyphen. The whole term, *e.g.* μ-chlorido, is separated from the rest of the name by hyphens, as in ammine-μ-chlorido-chlorido, *etc*., or by parentheses if more complex ligands are involved. If the bridging ligand occurs more than once and multiplicative prefixes are employed, the presentation is modified, as in tri-μ-chlorido-chlorido, *etc.*, or as in bis(μ-diphenylphosphido), *etc*. if more complex ligands are involved. The kappa nomenclature can be used when it is necessary to specify which central atoms are bridged and through which donor atoms (see Example 4 of Section IR-9.2.5.5.)

The bridging index, the number of coordination centres connected by a bridging ligand, is indicated by a right subscript, μ_n, where $n > 2$. The bridging index 2 is not normally indicated.

Bridging ligands are listed in alphabetical order along with the other ligands, but a bridging ligand is cited before a corresponding non-bridging ligand, as with di-μ-chlorido-tetrachlorido, unless structural information is being provided.

Multiple bridging is listed in descending order of complexity, *e.g.* μ_3-oxido-di-μ-oxido-trioxido. For ligand names requiring enclosing marks, μ is contained within those marks.

IR-9.2.5.3 *Metal-metal bonding*

Metal-metal bonding may be indicated in names by placing italicized atomic symbols of the appropriate metal atoms, separated by an 'em' dash and enclosed in parentheses, after the list of central atoms and before the ionic charge. The symbols are placed in the same order as the central atoms appear in the name (*i.e.* according to Table VI, with the first element reached when following the arrow being placed last). The number of such metal-metal bonds is indicated by an arabic numeral placed before the first element symbol and separated from it by a space. For the purpose of nomenclature, no distinction is made between different metal-metal bond orders.

Examples:

1. $[Br_4ReReBr_4]^{2-}$
   bis(tetrabromidorhenate)(*Re—Re*)(2−)

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

3. $[(OC)_5\overset{1}{Re}\overset{2}{Co}(CO)_4]$
   nonacarbonyl-1κ^5*C*,2κ^4*C*-rheniumcobalt(*Re—Co*)

4. $Cs_3[Re_3Cl_{12}]$
   caesium dodecachlorido-*triangulo*-trirhenate(3 *Re—Re*)(3−)

IR-9.2.5.4 *Symmetrical dinuclear entities*

The order of ligands and central atoms may be modified if the symmetry of the entity permits simpler names to be formed by employing multiplicative prefixes.

Examples:

1. $[\{Cr(NH_3)_5\}_2(\mu\text{-}OH)]^{5+}$
   μ-hydroxido-bis(pentaamminechromium)(5+)

2. $[\{PtCl(PPh_3)\}_2(\mu\text{-}Cl)_2]$
   di-μ-chlorido-bis[chlorido(triphenylphosphane)platinum]

3. $[\{Fe(NO)_2\}_2(\mu\text{-}PPh_2)_2]$
   bis(μ-diphenylphosphanido)bis(dinitrosyliron)

IR-9.2.5.5 *Unsymmetrical dinuclear entities*

The name of an unsymmetrical dinuclear species will result from following the general rules described in Section IR-9.2.5.1. These will give an alphabetical list of ligands followed by a priority list of central atoms (derived from the position of the central atoms in Table VI).

In Example 1 below, iridium is reached last on following the arrow shown in Table VI and is therefore listed before mercury in the name. It is also given priority number 1.

More detailed structural information is provided by including the kappa symbols for each ligand. This allows the donor atoms to be specified using the donor atom symbol immediately to the right of the kappa symbol. Placing the central atom priority number to the left of the kappa symbol specifies the central atom to which ligands are attached.

In cases where the central atoms are the same but have different coordination environments, the priority number is assigned by identifying the first point in the name where the ligands are not evenly distributed between the central atoms. Therefore, the central atom with the greater number of ligands earlier in the name has priority. Thus, in Example 2 the chromium atom with five of the nine ammine ligands attached is given priority number 1.

Bridging is indicated by the prefix μ and where bridging is accomplished by different atoms of the same group, the ligating locants and symbols are separated by a colon, *e.g.* -μ-nitrito-1κ*N*:2κ*O*-. In general, the hierarchy of punctuation marks is comma lower than colon lower than semi-colon but in this context the colon is used only to indicate bridging. Thus, in Example 5, both the comma and the semicolon appear since the bpy ligands are not involved in bridging and the modified hierarchy of marks must be applied.

Examples:

1. $[\{\overset{1}{Ir}Cl_2(CO)(PPh_3)_2\}(\overset{2}{Hg}Cl)]$

carbonyl-1κ*C*-trichlorido-1κ^2*Cl*,2κ*Cl*-bis(triphenylphosphane-1κ*P*)iridiummercury(*Ir*—*Hg*)

2. $[\overset{1}{\mathrm{Cr}}(NH_3)_5(\mu\text{-}OH)\overset{2}{\mathrm{Cr}}(NH_3)_4(NH_2Me)]^{5+}$

   nonaammine-1κ^5*N*,2κ^4*N*-μ-hydroxido-(methanamine-2κ*N*)dichromium(5+)

3. $[\{Co(NH_3)_3\}_2(\mu\text{-}NO_2)(\mu\text{-}OH)_2]^{3+}$

   di-μ-hydroxido-μ-nitrito-κ*N*:κ*O*-bis(triamminecobalt)(3+)

4. $[(H_3N)_3\overset{1}{\mathrm{Co}}(\mu\text{-}OH)_2(\mu\text{-}NO_2)\overset{2}{\mathrm{Co}}(py)(NH_3)_2]^{3+}$

   pentaammine-1κ^3*N*,2κ^2*N*-di-μ-hydroxido-μ-nitrito-1κ*N*:2κ*O*-(pyridine-2κ*N*)dicobalt(3+)

5. $[(bpy)(H_2O)\overset{1}{\mathrm{Cu}}(\mu\text{-}OH)_2\overset{2}{\mathrm{Cu}}(bpy)(SO_4)]$

   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)

6. $[\{Cu(py)\}_2(\mu\text{-}O_2CMe)_4]$

   tetrakis(μ-acetato-κ*O*:κ*O*')bis[(pyridine)copper(II)]

IR-9.2.5.6 *Trinuclear and larger structures*

The structural nomenclature of more complex polynuclear entities is based on the description of the central or fundamental structural unit and a logical procedure for numbering the atoms. Only the metal atoms are considered for this purpose. For nonlinear clusters, descriptors such as *tetrahedro* and *dodecahedro* are used to describe a central structural unit (CSU). However, synthetic chemistry has now advanced far beyond the range of the limited CSU set associated with this usage (see below) and these descriptors should only be used for simple cases.

A more comprehensive CSU descriptor and a numbering system, the CEP (Casey, Evans, Powell) system, has been developed specifically for fully triangulated polyboron polyhedra (deltahedra).[8] The CEP descriptors are systematic alternatives to the traditional descriptors for fully triangulated polyhedra (deltahedra) and are listed in Table IR-9.1.

Table IR-9.1 Structural descriptors

Number of atoms in CSU	*Descriptor*	*Point group*	*CEP descriptor*
3	*triangulo*	D_{3h}	
4	*quadro*	D_{4h}	
4	*tetrahedro*	T_d	[T_d-(13)-Δ^4-*closo*]
5		D_{3h}	[D_{3h}-(131)-Δ^6-*closo*]
6	*octahedro*	O_h	[O_h-(141)-Δ^8-*closo*]
6	*triprismo*	D_{3h}	
8	*antiprismo*	S_6	
8	*dodecahedro*	D_{2d}	[D_{2d}-(2222)-Δ^6-*closo*]
8	*hexahedro (cube)*	O_h	
12	*icosahedro*	I_h	[I_h-(1551)-Δ^{20}-*closo*]

Numbering of the CSU is based on locating a reference axis and planes of atoms perpendicular to the reference axis. The reference axis is the axis of highest rotational symmetry. Select that end of the reference axis with a single atom (or smallest number of atoms) in the first plane to be numbered. Orient the CSU so that the first position to receive a locant in the first plane with more than one atom is in the twelve o'clock position. Assign locant numbers to the axial position or to each position in the first plane, beginning at the twelve o'clock position and moving in either the clockwise or anticlockwise direction.

From the first plane move to the next position and continue numbering in the same direction (clockwise or anticlockwise), always returning to the twelve o'clock position or the position nearest to it in the forward direction before assigning locants in that plane. Continue numbering in this manner until all positions are numbered.

A complete discussion of numbering deltahedra may be found elsewhere.[8] The complete descriptor for the CSU should appear just before the central atom list. Where structurally significant, metal-metal bonds may be indicated (see Section IR-9.2.5.3).

IR-9.2.5.7 *Polynuclear clusters: symmetrical central structural units*

Central structural units may be identified specifically and numbered for nomenclature as described in Section IR-9.2.5.6. However, many symmetrical CSUs may not require a full set of locants in the name because compounds based upon them do not exhibit isomerism.

Locants for bridging ligands are cited as for dinuclear entities. Compound locants will at times be necessary for monoatomic bridges in more complicated polynuclear entities. For these entities the locants are cited before the ligand indicator κ and separated by a colon, *e.g.* tri-μ-chlorido-1:2κ^2*Cl;*1:3κ^2*Cl*;2:3κ^2*Cl*- indicates that there are three bridging chloride ligands and they bridge between atoms 1 and 2, 1 and 3, and 2 and 3 in the central atom list at the end of the name. Note that because of the use of the colon, sets of bridge locants are separated by semicolons. This practice applies the hierarchy of punctuation marks cited in Section IR-9.2.5.5.

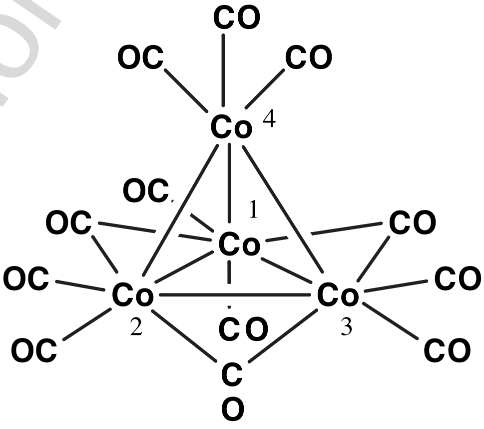
Examples:

1. $[\{Co(CO)_3\}_3(\mu_3\text{-}CBr)]$
   (μ_3-bromomethanetriido)-nonacarbonyl-*triangulo*-tricobalt(3 *Co—Co*),
   or (μ_3-bromomethanetriido)*triangulo*-tris(tricarbonylcobalt)(3 *Co—Co*)

2. $Cs_3[Re_3Cl_{12}]$
   caesium dodecachlorido-*triangulo*-trirhenate(3 *Re—Re*)(3−)

3. $[Cu_4(\mu_3\text{-}I)_4(PEt_3)_4]$
   tetra-μ_3-iodido-tetrakis(triethylphosphane)-*tetrahedro*-tetracopper, or
   tetra-μ_3-iodido-tetrakis(triethylphosphane)[T_d-(13)-Δ^4-*closo*]tetracopper

4. $[Co_4(CO)_{12}]$



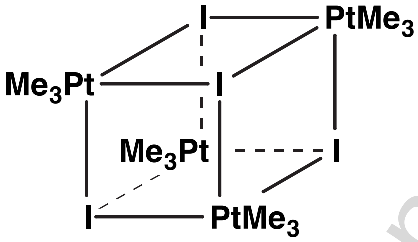
tri-μ-carbonyl-1:2κ^2*C*;1:3κ^2*C*;2:3κ^2*C*-nonacarbonyl-
1κ^2*C*,2κ^2*C*,3κ^2*C*,4κ^3*C*[Td-(13)-Δ4-*closo*]tetracobalt(6 *Co—Co*)

The compound may also be named by using chain and ring nomenclature (see Section IR-7.5 and Section II-5.3.3.3.6 of Ref. 9).

5. $[Mo_6S_8]^{2-}$

octa-μ_3-sulfido-*octahedro*-hexamolybdate (2−), or
octa-μ_3-sulfido-[O_h-(141)-Δ^8-*closo*]hexamolybdate(2−)

6.



tetra-μ_3-iodido-tetrakis[trimethylplatinum(IV)], or
tetra-μ_3-iodido-dodecamethyl-1κ^3C,2κ^3C,3κ^3C,4κ^3C-*tetrahedro*-tetraplatinum(IV), or
tetra-μ_3-iodido-dodecamethyl-1κ^3C,2κ^3C,3κ^3C,4κ^3C-[T_d-(13)-Δ^4-*closo*]tetraplatinum(IV)

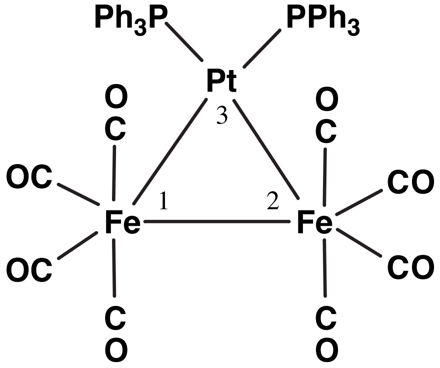
7. $[\mathrm{Be_4(\mu\text{-}O_2CMe)_6(\mu_4\text{-}O)}]$

hexakis(μ-acetato-κO:$\kappa O'$)-μ_4-oxido-*tetrahedro*-tetraberyllium, or
hexakis(μ-acetato-κO:$\kappa O'$)-μ_4-oxido-[T_d-(13)-Δ^4-*closo*]tetraberyllium

8. $[\mathrm{(HgMe)_4(\mu_4\text{-}S)}]^{2+}$

μ_4-sulfido-tetrakis(methylmercury)(2+), or
tetramethyl-1κC,2κC,3κC,4κC-μ_4-sulfido-*tetrahedro*-tetramercury(2+), or
tetramethyl-1κC,2κC,3κC,4κC-μ_4-sulfido[T_d-(13)-Δ^4-*closo*]tetramercury(2+)

9.



octacarbonyl-1κ^4C,2κ^4C-bis(triphenylphosphane-3κP)-*triangulo*-
diironplatinum(*Fe*—*Fe*)(2 *Fe*—*Pt*)

IR-9.2.5.8 *Polynuclear clusters: unsymmetrical central structural units*

Central atoms in chain, branched-chain, and cyclic polynuclear structures are numbered consecutively from one end along the path containing the greatest number of central atoms. For chains, the end from which numbering should begin is identified in the following way.

(i) Beginning at each end of the chain, and working towards the centre, locate:

(a) the first points of central atom difference or, if the central atoms are symmetrically distributed through the chain;

(b) the first central atoms at which there is a difference in the number of ligands attached to a central atom or, if the ligands are symmetrically distributed through the chain;

(c) the first central atoms where different types of ligand are attached.

(ii) Compare the points of difference and begin numbering at the end of the chain closer to:

(a) the central atom that is reached last on following the arrow shown in Table VI (*i.e.* the central atom that appears first in the list of central atoms in the name, see Section IR-9.2.5.1);

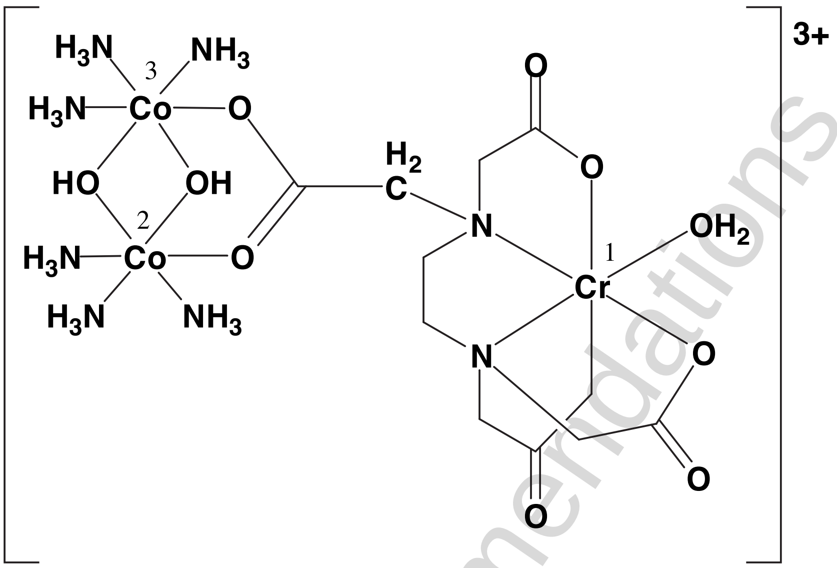
(b) the central atom with more ligands;

(c) the central atom with the ligand that comes first in the alphabetical order of ligands.

When needed, the locant precedes the atom name in the central atom list, within the name (see Example 1). The ligand indicator kappa, κ, (with central atom locant and italicized donor atom symbol) is used where necessary to indicate the positions of the ligating atoms.

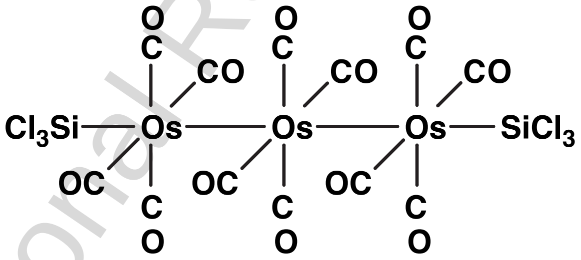
Examples:

1.



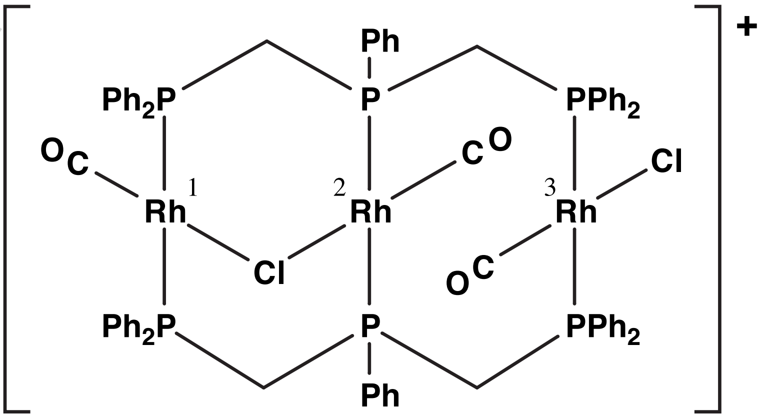
hexaammine-2κ^3*N*,3κ^3*N*-aqua-1κ*O*-{μ$_3$-(1,2-ethanediyldinitrilo-1κ^2*N*,*N*′)-tetraacetato-1κ^3*O*^{1},*O*^{2},*O*^{3}:2κ*O*^{4}:3κ*O*$^{4'}$}-di-μ-hydroxido-2:3κ^4*O*-chromiumdicobalt(3+)

2. $[Os_3(CO)_{12}(SiCl_3)_2]$



dodecacarbonyl-1κ^4*C*,2κ^4*C*,3κ^4*C*-bis(trichlorosilyl)-1κ*Si*,3κ*Si*-triosmium(2 *Os*—*Os*)

3.



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+)

or, using the preferred IUPAC name[1] for the phosphine ligand:

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

Numbering cyclic structures requires location of a starting point and a direction for the numbering. The central atom starting point is identified by comparing all the central atoms in the cyclic portion of the molecule. The starting point will be:

(i) the central atom that is reached last on following the arrow in Table VI (*i.e.* the central atom that appears first in the list of central atoms in the name, see Section IR-9.2.5.1) and, if there is more than one such central atom,

(ii) the atom with more ligands attached and, if the number of ligands is the same,

(iii) the atom with the greatest number of alphabetically preferred ligands.

If these highest ranked central atoms are still identical then the choice is made by comparing the adjacent central atoms in the ring to one another, according to the criteria above, until a difference is established.

The direction of numbering from the starting point is determined by making this same comparison of adjacent central atoms, but in this case comparing those that lie in each direction from the chosen starting point.

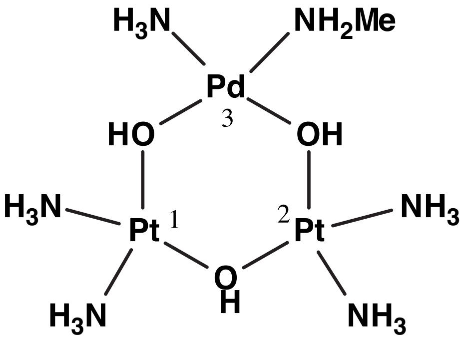
The prefix '*cyclo*', italicized and cited before all ligands, may be used for monocyclic compounds.

Examples:

6. $[Pt_3(NH_3)_6(\mu\text{-}OH)_3]^{3+}$

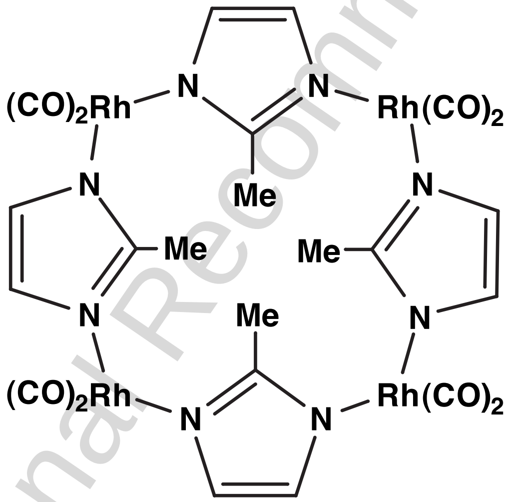
cyclo-tri-μ-hydroxido-tris(diammineplatinum)(3+), or
hexaamminetri-μ-hydroxido-*triangulo*-triplatinum(3 +)

7.



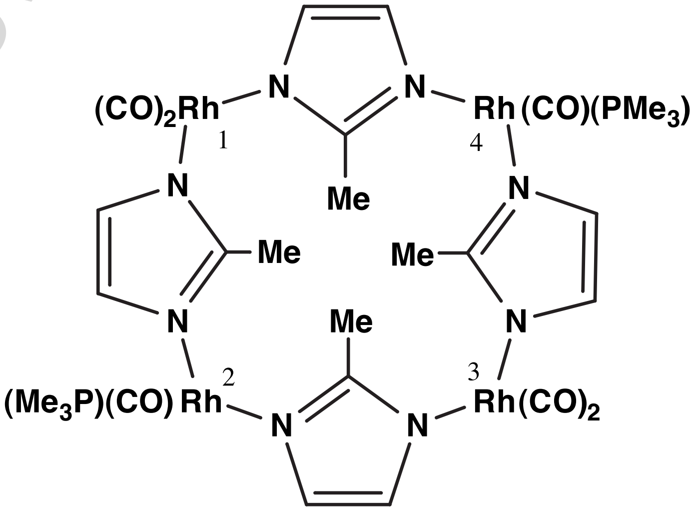
cyclo-pentaammine-1κ^{2}*N*,2κ^{2}*N*,3κ*N*-tri-μ-hydroxido-1:2κ^{2}*O*;1:3κ^{2}*O*;2:3κ^{2}*O*-(methanamine-3κ*N*)diplatinumpalladium(3+)

8.



cyclo-tetrakis(μ-2-methylimidazolato-κ*N*^{1}:κ*N*^{3})tetrakis(dicarbonylrhodium)

9.



cyclo-hexacarbonyl-1κ^2C,2κC,3κ^2C,4κC-tetrakis(μ-2-methylimidazolato)-1:2κ$^2N^1$:N^3;1:4κ$^2N^1$:N^3;2:3κ$^2N^1$:N^3;3:4κ$^2N^1$:N^3-bis(trimethylphosphane)-2κP,4κP-tetrarhodium

When the prefix *cyclo* is used in the names of metal-metal bonded entities, symbols indicating the presence of the metal-metal bonds are required.

Example:

10. $[Os_3(CO)_{12}]$
cyclo-dodecacarbonyl-1κ^4C,2κ^4C,3κ^4C-triosmium(3 *Os—Os*)

IR-9.3 DESCRIBING THE CONFIGURATION OF COORDINATION COMPOUNDS

IR-9.3.1 Introduction

Once the constitution of a compound has been defined, it remains to describe the spatial relationships between the structural components of the molecule. Molecules that differ only in the spatial distribution of the components are known as stereoisomers. Stereoisomers that are mirror images of one another are called enantiomers (sometimes these have been called optical isomers), while those that are not are called diastereoisomers (or geometrical isomers). This is an important distinction in chemistry as, in general, diastereoisomers exhibit different physical and spectroscopic properties from one another, while enantiomers exhibit identical properties (except in the presence of other chiral entities). It is instructive to consider an everyday analogy in order to establish how the configuration of a molecule (and the embedded spatial relationships) can be described.

Using the terminology introduced above, left and right hands may be regarded as enantiomers of one another, since they are different (non-superimposable), but they are mirror images of each other. In both cases the thumbs are adjacent to the index finger, and the components of each hand are similarly disposed relative to all the other parts of that hand. If the thumb and index finger of a right hand were to be exchanged, the resulting hand could be considered to be a diastereoisomer of the normal right hand (and it too would have an enantiomer, resulting from a similar exchange on a left hand). The key point is that the relative positions of the components of diastereoisomers (the normal right hand and the modified one) are different.

In order to describe the hand fully the components (four fingers, one thumb, and the central part of the hand) must be identified, the points of attachment available on the hand, and the relative positions of the fingers and thumb around the hand, must be described and whether the hand is 'left' or 'right' must be identified. The last three steps deal with the stereochemistry of the hand.

In the case of a coordination compound, the names and formula describe the ligands and central atom(s). Describing the configuration of such a coordination compound requires consideration of three factors:

(i) coordination geometry – identification of the overall shape of the molecule;

(ii) relative configuration – description of the relative positions of the components of the molecule, *i.e.* where the ligands are placed around the central atom(s) in the identified geometry;

(iii) absolute configuration – identification of which enantiomer is being specified (if the mirror images are non-superimposable).

The next three sections deal with these steps in turn. A more detailed discussion of the configuration of coordination compounds can be found elsewhere.[10]

IR-9.3.2 Describing the coordination geometry

IR-9.3.2.1 *Polyhedral symbol*

Different geometrical arrangements of the atoms attached to the central atom are possible for all coordination numbers greater than one. Thus, two-coordinate species may involve a linear or a bent disposition of the ligands and central atom. Similarly, three-coordinate species may be trigonal planar or trigonal pyramidal, and four-coordinate species may be square planar, square pyramidal, or tetrahedral. The coordination polyhedron (or polygon in planar molecules) may be denoted in the name by an affix called the *polyhedral symbol*. This descriptor distinguishes isomers differing in the geometries of their coordination polyhedra.

The polyhedral symbol indicates the geometrical arrangements of the coordinating atoms about the central atom. This symbol must be assigned before any other stereochemical features can be considered. It consists of one or more capital italic letters derived from common geometric terms which denote the idealized geometry of the ligands around the coordination centre, and an arabic numeral that is the coordination number of the central atom.

Distortions from idealized geometries commonly occur. However, it is normal practice to relate molecular structures to idealized models. The polyhedral symbol is used as an affix, enclosed in parentheses and separated from the name by a hyphen. The polyhedral symbols for the most common geometries for coordination numbers 2 to 9 are given in Table IR-9.2 and the corresponding structures and/or polyhedra are shown in Table IR-9.3.

Table IR-9.2 Polyhedral symbols[a]

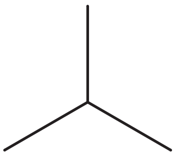
Coordination polyhedron	Coordination number	Polyhedral symbol
linear	2	*L*-2
angular	2	*A*-2
trigonal plane	3	*TP*-3
trigonal pyramid	3	*TPY*-3
T-shaped	3	*TS*-3
tetrahedron	4	*T*-4
square plane	4	*SP*-4
square pyramid	4	*SPY*-4
see-saw	4	*SS*-4
trigonal bipyramid	5	*TBPY*-5
square pyramid	5	*SPY*-5
octahedron	6	*OC*-6
trigonal prism	6	*TPR*-6
pentagonal bipyramid	7	*PBPY*-7
octahedron, face monocapped	7	*OCF*-7
trigonal prism, square face monocapped	7	*TPRS*-7
cube	8	*CU*-8
square antiprism	8	*SAPR*-8
dodecahedron	8	*DD*-8
hexagonal bipyramid	8	*HBPY*-8
octahedron, *trans*-bicapped	8	*OCT*-8
trigonal prism, triangular face bicapped	8	*TPRT*-8
trigonal prism, square face bicapped	8	*TPRS*-8
trigonal prism, square face tricapped	9	*TPRS*-9
heptagonal bipyramid	9	*HBPY*-9

[a] Strictly, not all geometries can be represented by polyhedra.

Table IR-9.3 Polyhedral symbols, geometrical structures and/or polyhedra

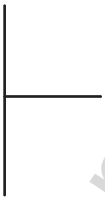
Three-coordination

trigonal plane	trigonal pyramid	T-shape



TP-3

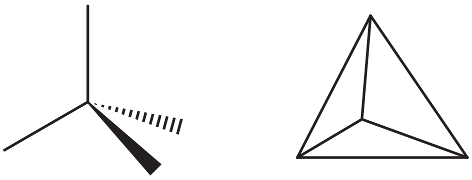
TPY-3



TS-3

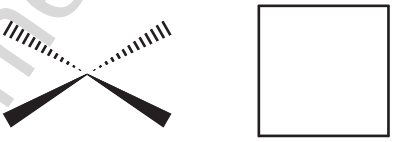
Four-coordination

tetrahedron



T-4

square plane

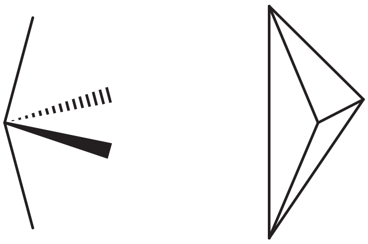


SP-4

square pyramid

SPY-4

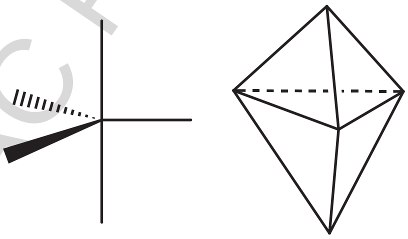
see-saw



SS-4

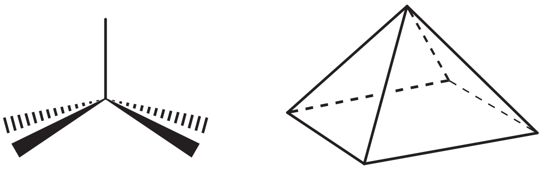
Five-coordination

trigonal bipyramid



TBPY-5

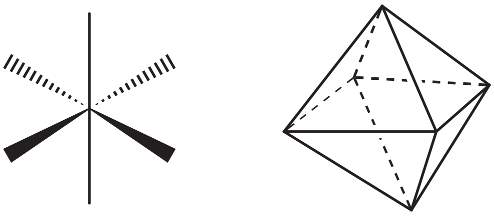
square pyramid



SPY-5

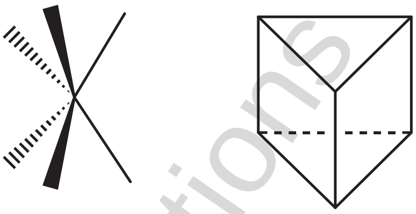
Six-coordination

octahedron



OC-6

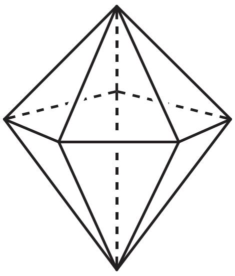
trigonal prism



TPR-6

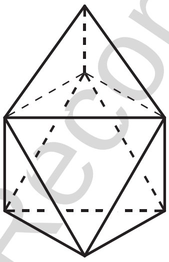
Seven-coordination

pentagonal
bipyramid



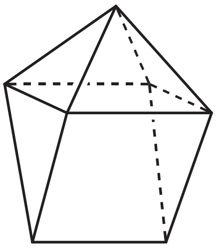
PBPY-7

octahedron, face
monocapped



OCF-7

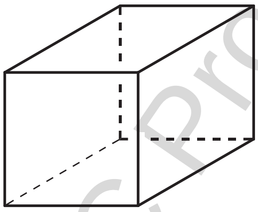
trigonal prism,
square face
monocapped



TPRS-7

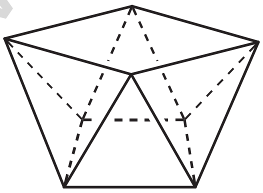
Eight-coordination

cube



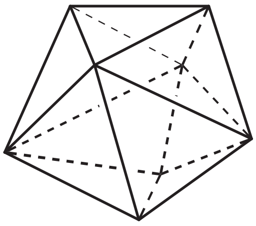
CU-8

square
antiprism



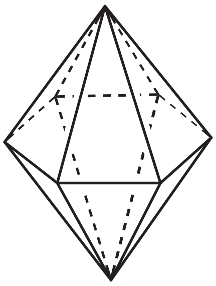
SAPR-8

dodecahedron



DD-8

hexagonal
bipyramid

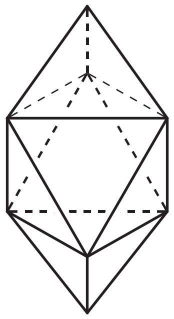


HBPY-8

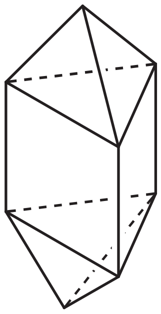
octahedron,
trans-bicapped

trigonal prism,
triangular face
bicapped

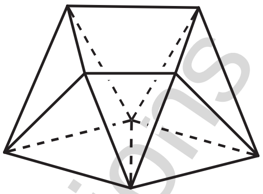
trigonal prism,
square face
bicapped



OCT-8



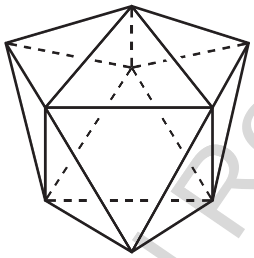
TPRT-8



TPRS-8

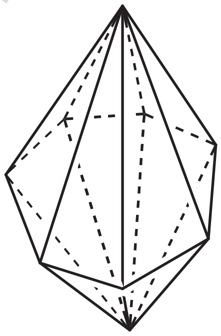
Nine-coordination

trigonal prism,
square face
tricapped



TPRS-9

heptagonal
bipyramid



HBPY-9

IR-9.3.2.2 *Choosing between closely related geometries*

For real molecules, the stereochemical descriptor should be based on the nearest idealized geometry. However, some idealized geometries are closely related (*e.g.* square planar – *SP*-4, four-coordinate square pyramidal – *SPY-4*, see-saw – *SS*-4, and tetrahedral – *T*-4; T-shaped – *TS*-3, trigonal planar – *TP*-3, and trigonal pyramidal – *TPY*-3) and care may therefore be required in making the choice.

The following approach is useful in determining the polyhedral symbol for four-coordinate structures. The key is to consider the locations of the central atom and the coordinating atoms in relation to each other. If all five atoms are in (or are close to being in) the same plane, then the molecule should be treated as square planar. If the four coordinating atoms are in a plane, but the central atom is significantly displaced from the plane, then the square pyramidal geometry is appropriate. If the four coordinating atoms do not lie in (or close to) a plane, then a polyhedron can be defined by joining all four coordinating atoms together with lines. If the central atom lies inside this polyhedron the molecule should be regarded as tetrahedral, otherwise, it should be regarded as having a see-saw structure.

T-shaped and trigonal planar molecules both have a central atom that lies in (or close to) the plane defined by the coordinating atoms. They differ in that the angles between the three coordinating atoms are approximately the same in the trigonal planar structure, while one angle is much larger than the other two in a T-shaped molecule. The central atom lies significantly out of the plane in a trigonal pyramidal structure.

IR-9.3.3 Describing relative configuration – distinguishing between diastereoisomers

IR-9.3.3.1 *General*

The placement of ligands around the central atom must be described in order to identify a particular diastereoisomer. There are a number of common terms (*e.g. cis, trans, mer and fac*) used to describe the relative locations of ligands in simple systems. However, they can be used only when a particular geometry is present (*e.g.* octahedral or square planar), and when there are only two kinds of donor atom present (*e.g.* Ma_2b_2 in a square planar complex, where M is a central atom and 'a' and 'b' are types of donor atom).

Several methods have been used to distinguish between diastereoisomers in more complex systems. Thus, stereoisomers resulting from the coordination of linear tetradentate ligands have often been identified as *trans*, *cis*-α, or *cis*-β,[11] and those resulting from coordination of macrocyclic tetradentate ligands have their own system.[12] The scope of most of these nomenclatures is generally quite limited, but a proposal with wider application in the description of complexes of polydentate ligands has been made recently.[13]

Clearly a general method is required in order to distinguish between diastereoisomers of compounds in which either other geometries or more than two kinds of donor atoms are present. The *configuration index* has been developed for this purpose. The next section outlines the method by which a configuration index is obtained for a compound, and the following sections give details for particular geometries. Commonly used terms are included when the appropriate geometry is being discussed.

IR-9.3.3.2 *Configuration index*

Once the coordination geometry has been specified by the polyhedral symbol, it becomes necessary to identify which ligands (or donor atoms) occupy particular coordination positions. This is achieved through the use of the configuration index which is a series of digits identifying the positions of the ligating atoms on the vertices of the coordination polyhedron. The individual configuration index has the property that it distinguishes between diastereoisomers. It appears within the parentheses enclosing the polyhedral symbol (see Section IR-9.3.2.1), following that symbol and separated from it by a hyphen.

Each donor atom must be assigned a priority number based on the rules developed by Cahn, Ingold and Prelog (the CIP rules).[14] These priority numbers are then used to form the configuration index for the compound. The application of the CIP rules to coordination compounds is discussed in detail in Section IR-9.3.5 but, in general, donor atoms that have a higher atomic number have higher priority than those that have a lower atomic number.

The presence of polydentate ligands may require the use of primes on some of the numbers in the configuration index. The primes are used to indicate either that donor atoms are not part of the same polydentate ligand as those that have unprimed priority numbers, or that the donor atoms belong to different parts of a polydentate ligand that are related by symmetry. A primed priority number means that that donor atom has lower priority than the same kind of donor atom without a prime on the priority number. More detail on the 'priming convention' can be found in Section IR-9.3.5.3.

IR-9.3.3.3 *Square planar coordination systems (SP-4)*

The terms *cis* and *trans* are used commonly as prefixes to distinguish between stereoisomers in square planar systems of the form [$\mathrm{Ma_2b_2}$], where M is the central atom, and 'a' and 'b' are different types of donor atom. Similar donor atoms occupy coordination sites adjacent to one another in the *cis* isomer, and opposite to one another in the *trans* isomer. The *cis-trans* terminology is not adequate to distinguish between the three isomers of a square planar coordination entity [Mabcd], but could be used, in principle, for an [$\mathrm{Ma_2bc}$] system (where the terms *cis* and *trans* would refer to the relative locations of the similar donor atoms). This latter use is not recommended.

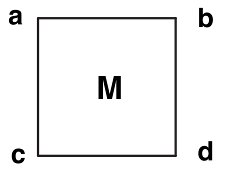
The configuration index for a square planar system is placed after the polyhedral symbol (*SP*-4). It is the single digit which is the priority number for the ligating atom *trans* to the ligating atom of priority number 1, *i.e.* the priority number of the ligand *trans* to the most preferred ligating atom.

Examples:

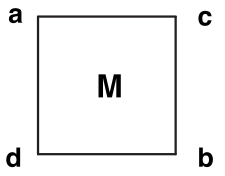
1.

Priority sequence: $a > b > c > d$

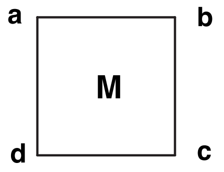
Priority number sequence: $1 < 2 < 3 < 4$



SP-4-4

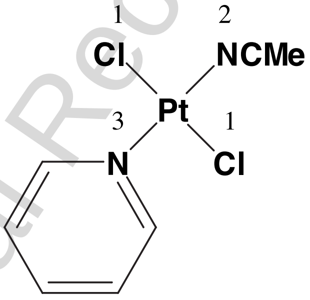


SP-4-2



SP-4-3

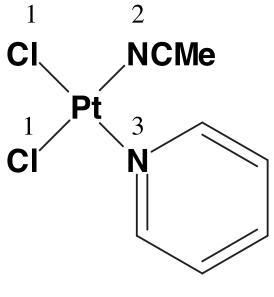
2.



(*SP*-4-1)-(acetonitrile)dichlorido(pyridine)platinum(II)

If there are two possibilities, as in Example 3, the configuration index is the priority number with the higher numerical value. Both the priority 2 ligand (acetonitrile) and the priority 3 ligand (pyridine) are *trans* to a priority 1 ligand (chloride). The higher numerical value (3) is chosen for the configuration index. This choice is sometimes referred to as having been made according to the principle of *trans* maximum difference, *i.e.* that the difference between the numerical values of the priority numbers of the ligands should be as large as possible.

3.



(*SP*-4-3)-(acetonitrile)dichlorido(pyridine)platinum(II)

IR-9.3.3.4 *Octahedral coordination systems (OC-6)*

The terms *cis* and *trans* are used commonly as prefixes to distinguish between stereoisomers in octahedral systems of the form [Ma_4b_2], where M is the central atom, and 'a' and 'b' are different types of donor atom. The 'b' donors occupy adjacent coordination sites in the *cis* isomer, and opposite coordination sites in the *trans* isomer (Example 1).

The terms *mer* (meridional) and *fac* (facial) are used commonly to distinguish between stereoisomers of complexes of the form [Ma_3b_3]. In the *mer* isomer (Example 2) the two groups of three similar donors each lie on a meridian of the coordination octahedron, in planes that also contain the central atom. In the *fac* isomer (Example 3) the two groups of three similar donors each occupy coordination sites on the corners of a face of the coordination octahedron.

The configuration index of an octahedral system follows the polyhedral symbol (*OC*-6) and consists of two digits. The first digit is the priority number of the ligating atom *trans* to the ligating atom of priority number 1, *i.e.* the priority number of the ligand *trans* to the most preferred ligating atom.

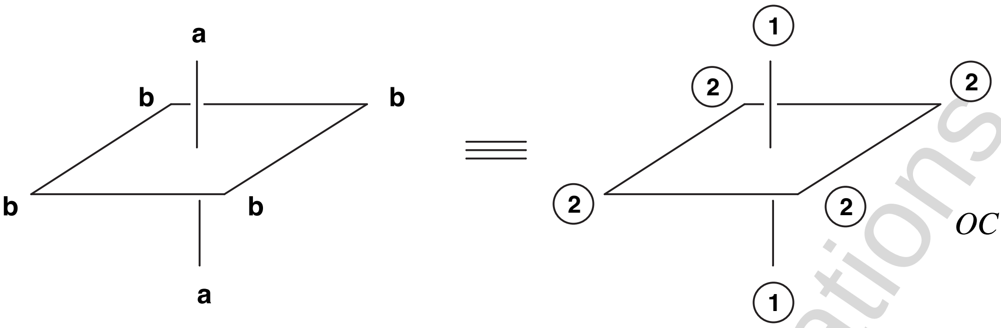
If there is more than one ligand of priority 1, then the first digit is the priority number of the *trans* ligand with the highest numerical value (remembering that a primed number will be of higher numerical value than the corresponding unprimed number).

These two ligating atoms, the priority 1 ligand and the (lowest priority) ligand *trans* to it, define the reference axis of the octahedron.

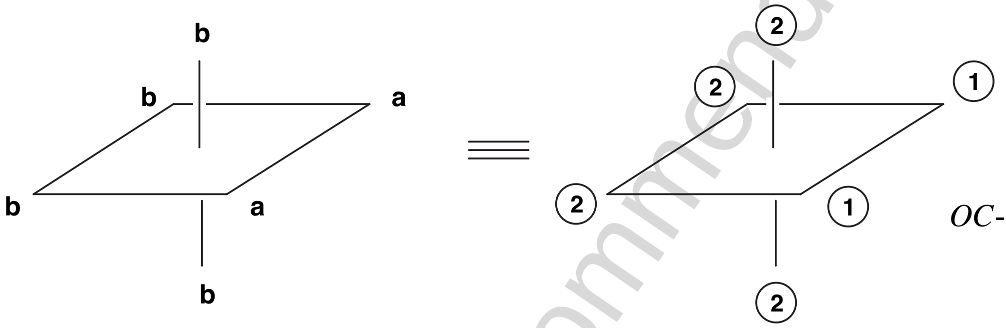
The second digit of the configuration index is the priority number of the ligating atom *trans* to the most preferred ligand in the plane that is perpendicular to the reference axis. If there is more than one of the highest priority ligand in the plane, the priority number of the *trans* ligand having the largest numerical value is selected.

Examples:

1.

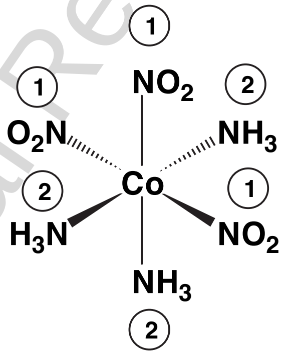


OC-6-12



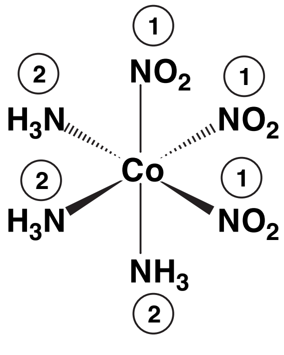
OC-6-22

2.



mer-$[Co(NH_3)_3(NO_2)_3]$ or
(*OC*-6-21)-triamminetrinitrito-κ^3*N*-cobalt(III)

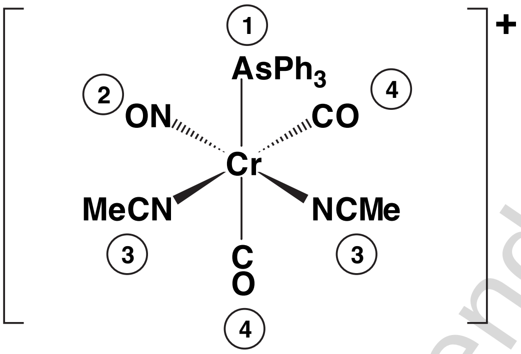
3.



fac-$[Co(NH_3)_3(NO_2)_3]$ or

(*OC*-6-22)-triamminetrinitrito-κ^3*N*-cobalt(III)

4.



(*OC*-6-43)-bis(acetonitrile)dicarbonylnitrosyl(triphenylarsane)chromium(1+)

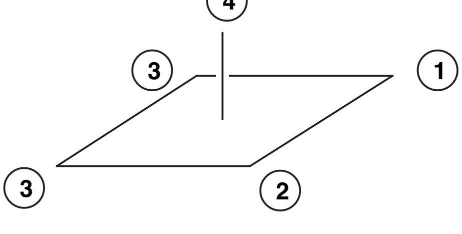
IR-9.3.3.5 *Square pyramidal coordination systems (SPY-4, SPY-5)*

The configuration index of an *SPY*-5 system consists of two digits. The first digit is the priority number of the ligating atom on the C_4 symmetry axis (the reference axis) of the idealized pyramid. The second digit is the priority number of the ligating atom *trans* to the ligating atom with the lowest priority number in the plane perpendicular to the C_4 symmetry axis. If there is more than one of the highest priority (most preferred) ligand in the perpendicular plane, then the second digit is chosen to have the highest numerical value (*i.e.* the less preferred ligand that is *trans* to a most preferred ligand).

The configuration index of an *SPY*-4 system is a single digit that is chosen in the same way as the second digit of *SPY*-5 systems. The configuration index of a four-coordinate square pyramidal system will therefore be the same as that for the square planar structure that would result from the ligands and the central atom being coplanar. The difference between the structures is described by the polyhedral symbol rather than by the configuration index.

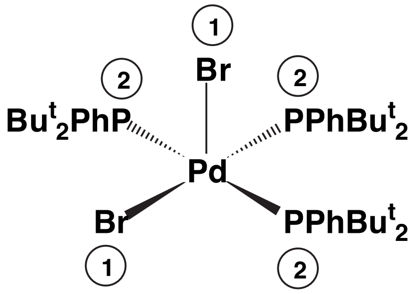
Examples:

1.



SPY-5-43

2.



(*SPY*-5-12)-dibromidotris[di-*tert*-butyl(phenyl)phosphane]palladium

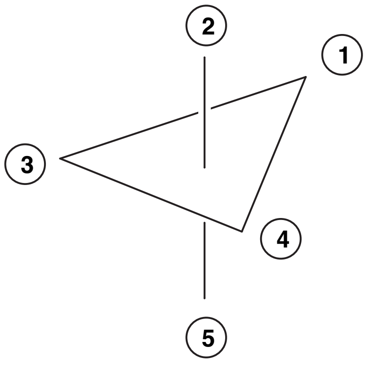
IR-9.3.3.6 *Bipyramidal coordination systems (TBPY-5, PBPY-7, HBPY-8, and HBPY-9)*

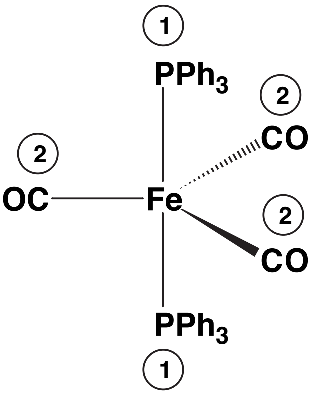
The configuration index for bipyramidal coordination systems follows the appropriate polyhedral symbol, and consists of two segments separated by a hyphen. The first segment has two digits which are the priority numbers of the ligating atoms on the highest order rotational symmetry axis, the reference axis. The lower number is cited first.

The second segment consists of the priority numbers of the ligating atoms in the plane perpendicular to the reference axis. (For the trigonal bipyramid, this segment of the configuration index is not required and is therefore omitted). The first digit is the priority number for the preferred ligating atom, *i.e.* the lowest priority number in the plane. The remaining priority numbers are cited in sequential order proceeding around the projection of the structure either clockwise or anticlockwise, in whichever direction gives the lower numerical sequence. The lowest numerical sequence is that having the lower number at the first point of difference when the numbers are compared digit by digit from one end to the other.

Examples:

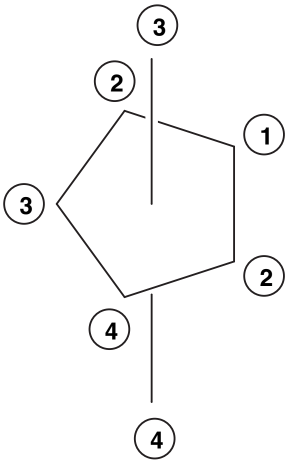
1. Trigonal bipyramid (*TBPY*-5)





TBPY-5-25 (*TBPY*-5-11)-tricarbonylbis(triphenylphosphane)iron

2. Pentagonal bipyramid (*PBPY*-7)



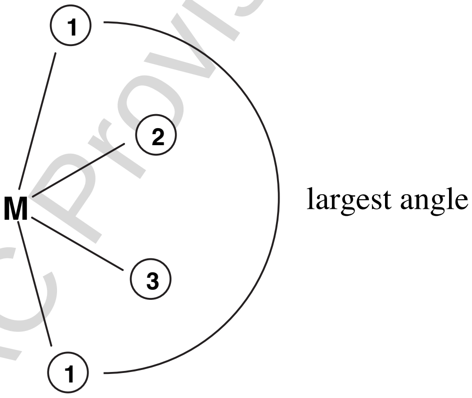
PBPY-7-34-12342 (not 12432)

IR-9.3.3.7 *T-shaped systems (TS-3)*

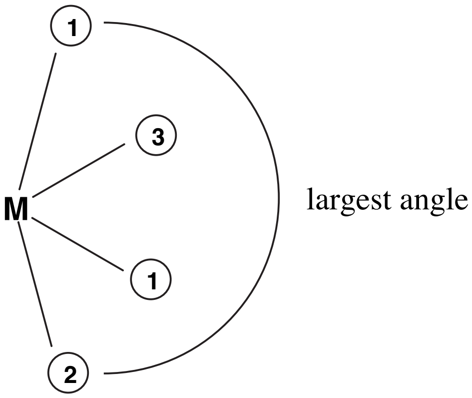
The configuration index for T-shaped systems follows the polyhedral symbol and consists of a single digit, the priority number of the ligand on the stem of the T (as opposed to the cross piece of the T).

IR-9.3.3.8 *See-saw systems (SS-4)*

The configuration index for see-saw systems consists of two digits, the priority numbers of the two ligands separated by the largest angle. The number of lower numerical value is cited first.



SS-4-11



SS-4-12

IR-9.3.4 Describing absolute configuration – distinguishing between enantiomers

IR-9.3.4.1 *General*

There are two well-established, but fundamentally different, systems for distinguishing between two enantiomers (stereoisomers that are mirror images of one another). The first, based on the chemical constitution of the compound, involves the *R*/*S* convention used for describing tetrahedral centres and the closely related *C*/*A* convention used for other polyhedra. The *R*/*S* and *C*/*A* conventions use the priority sequence referred to in Section IR-9.3.3.2, and detailed in Section IR-9.3.5, where the ligands are assigned a priority number based (usually) on the atomic number of the donor atoms and their substituents.

The second is based on the geometry of the molecule, makes use of the skew-line convention, and applies only to octahedral complexes. The two enantiomers are identified by the symbols Δ and Λ in this system. The *C*/*A* nomenclature is not required for those chelate complexes where the skew-line convention is completely unambiguous (see Sections IR-9.3.4.11 - 9.3.4.14).

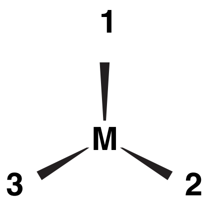
IR-9.3.4.2 *The* R/S *convention for tetrahedral centres*

The convention used to describe the absolute configurations of tetrahedral centres was originally developed for carbon atom centres (see Ref. 14 and Section P-91 of Ref. 1) but can be used for any tetrahedral centre. There is no need to alter the rules in treating tetrahedral metal complexes.

The symbol *R* is assigned if the cyclic sequence of priority numbers, proceeding from highest priority, is clockwise when the viewer is looking down the vector from the tetrahedral centre to the least preferred substituent (the substituent having the priority number with the highest numerical value, *i.e.* 4), as in Example 1. An anticlockwise cyclic sequence is assigned the symbol *S* (Example 2).

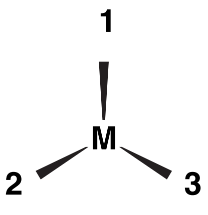
Examples:

1.



R

2.

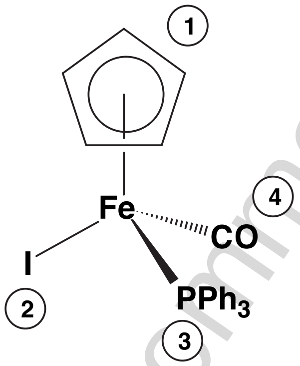


S

This system is most often used in conjunction with ligand configuration but can be applied equally to tetrahedral metal centres. It has also been useful for pseudotetrahedral organometallic complexes when, for example, cyclopentadienyl ligands are treated as if they were monodentate ligands of high priority.

Example:

3.



T-4-*S*

IR-9.3.4.3 *The* R/S *convention for trigonal pyramidal centres*

Molecules containing a trigonal pyramidal centre (*TPY*-3) may exist as a pair of stereoisomers. The configuration of this centre can be described in a similar way to that of a tetrahedral centre. This is achieved through notional placement of a 'phantom atom' of low priority in the coordination site that would create a tetrahedral centre from a trigonal pyramidal centre. The centre can then be identified as *R* or *S* by the methods described above.

The use of some bonding theories leads to the placement of a lone pair on a trigonal pyramidal centre. If this is done, the absolute configuration of the centre is also described by the *R*/*S* convention, in this case by placing the 'phantom atom' in the site that is occupied by the lone pair. Examples of this practice may be found in the description of absolute configurations for sulfoxides in which the alkyl substituents are different.

IR-9.3.4.4 *The* C/A *convention for other polyhedral centres*

The *R*/*S* convention makes use of priority numbers for the determination of chirality at tetrahedral centres, as detailed above. The same principles are readily extendable to geometries other than tetrahedral.[15] However, in order to avoid confusion, and to emphasize the unique aspects of the priority sequence systems as applied to coordination polyhedra, the symbols *R* and *S* are replaced by the symbols *C* and *A* when applied to other polyhedra.

The procedure for arriving at ligating atom priorities is detailed in Section IR-9.3.5. Once the ligand priorities have been assigned, the reference axis (and direction) appropriate to the geometry is identified. The priority numbers of the ligands coordinated in the plane perpendicular to the reference axis are then considered, viewing from the axial ligand of higher priority.

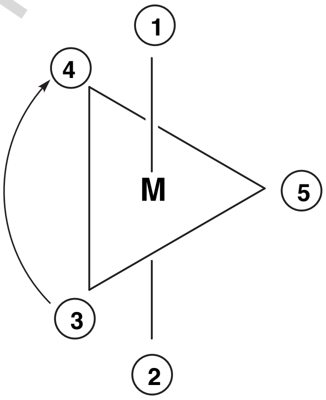
Beginning with the highest priority ligand in the plane perpendicular to the reference axis, the clockwise and anticlockwise sequences of priority numbers are compared, and that with the lower number at the first point of difference is chosen. If the chosen sequence results from a clockwise reading of the priority numbers, then the structure is given the chirality symbol *C*, otherwise it is given the symbol *A*.

IR-9.3.4.5 *The* C/A *convention for trigonal bipyramidal centres*

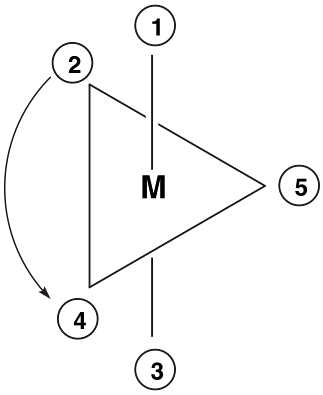
The procedure is similar to that used for tetrahedral systems in the *R*/*S* convention, but it is modified because of the presence of a unique reference axis (running through the two axial donor atoms and the central atom).

The structure is oriented so that the viewer looks down the reference axis, with the more preferred ligand (having a priority number with lower numerical value) closer to the viewer. Accordingly, the axial ligand with the lower priority lies beyond the central atom. Using this orientation, the priority sequence of the three ligating atoms in the trigonal plane is examined. If the sequence proceeds from the highest priority to the lowest priority in a clockwise fashion, the chirality symbol *C* is assigned. Conversely, if the sequence from highest to lowest priority (from lowest numerical index to highest numerical index) is anticlockwise, the symbol *A* is assigned.

Examples:



1. Chirality symbol = *C*



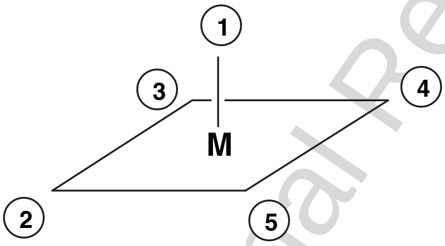
2. Chirality symbol = *A*

IR-9.3.4.6 *The* C/A *convention for square pyramidal centres*

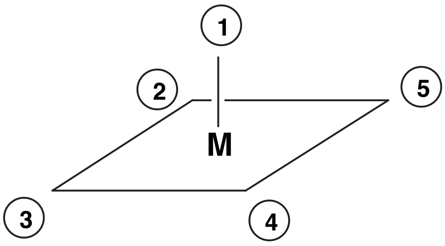
A procedure similar to that described in Section IR-9.3.4.4 is used for square pyramidal structures. In the case of *SPY*-5 systems, the polyhedron is oriented so that the viewer looks along the formal C_4 axis, from the axial ligand toward the central atom. The priority numbers of the ligands in the perpendicular plane are then considered, beginning with the highest priority ligand (the one having the priority number of lowest numerical value). The clockwise and anticlockwise sequences of priority numbers are compared, and the structure is assigned the symbol *C* or *A* according to whether the clockwise (*C*) or anticlockwise (*A*) sequence is lower at the first point of difference.

The chirality of an *SPY*-4 system is defined in a similar way. In this case, the viewer looks along the formal C_4 axis in such a way that the ligands are further away than the central atom. The priority numbers are then used to assign the symbol *C* or *A*, as for the *SPY*-5 system.

Examples:



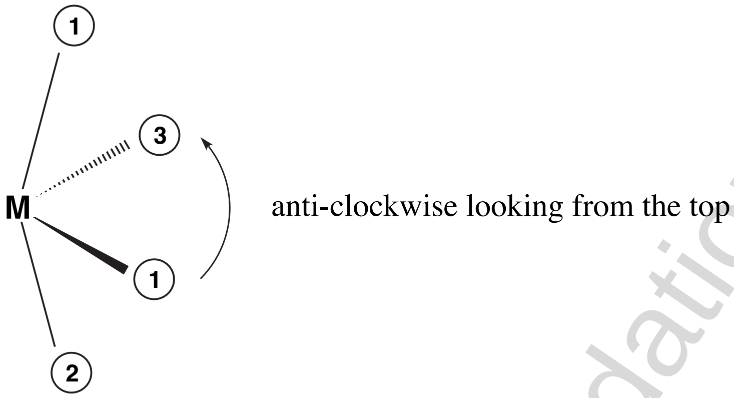
1. Chirality symbol = *C*



2. Chirality symbol = *A*

IR-9.3.4.7 *The* C/A *convention for see-saw centres*

The absolute configurations of see-saw complexes can be described using the *C*/*A* system. The configuration index for see-saw systems consists of two digits, the priority numbers of the two ligands separated by the largest angle. The higher priority ligand of these two is identified and used as a point from which to view the two ligands not involved in the configuration index. If moving from the higher priority ligand to the lower (through the smaller angle) entails making a clockwise motion, the absolute configuration is assigned *C*. An anti-clockwise direction results in the absolute configuration *A*.



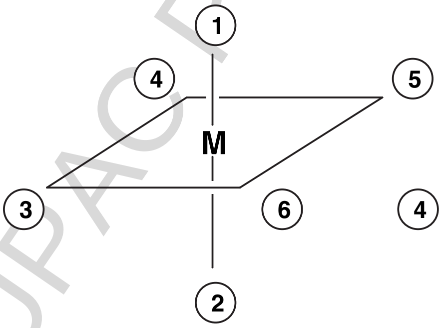
SS-4-12-*A*

IR-9.3.4.8 *The* C/A *convention for octahedral centres*

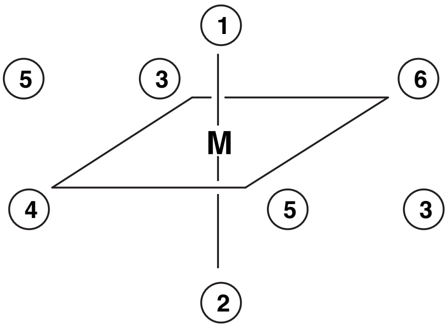
The absolute configurations of some octahedral complexes can be described using either the skew-line reference system (Section IR-9.3.4.11) or the *C*/*A* system. The first is used more commonly, but the *C*/*A* system is more general and may be used for most complexes. The skew-line reference system is only applicable to tris(bidentate), bis(bidentate) and closely related systems.

The reference axis for an octahedral centre is that axis containing the ligating atom of CIP priority 1 and the *trans* ligating atom of lowest possible priority (highest numerical value) (see Section IR-9.3.3.4). The atoms in the coordination plane perpendicular to the reference axis are viewed from the ligand having that highest priority (CIP priority 1) and the clockwise and anticlockwise sequences of priority numbers are compared. The structure is assigned the symbol *C* or *A*, according to whether the clockwise (*C*) or anticlockwise (*A*) sequence is lower at the first point of difference.

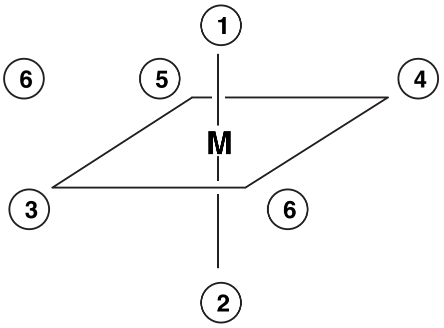
Examples:



1. Chirality symbol = *C*



2. Chirality symbol = *A*

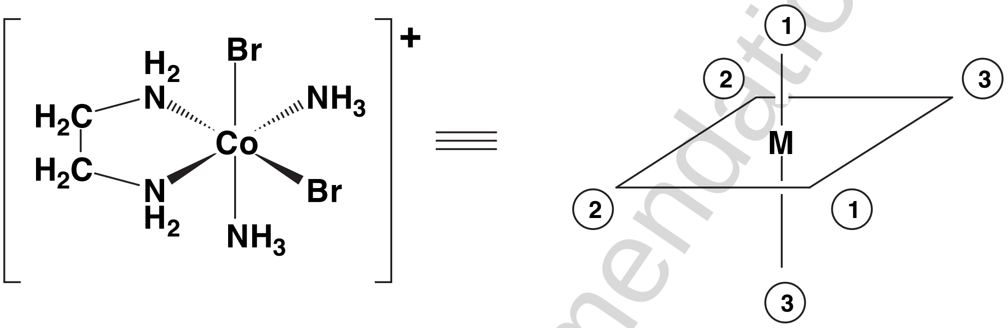


3. Chirality symbol = *C*

Example 4 shows the compound $[CoBr_2(en)(NH_3)_2]^+$ which has the polyhedral symbol *OC*-6 and the configuration index 32. The chirality symbol is *C*.

Example:

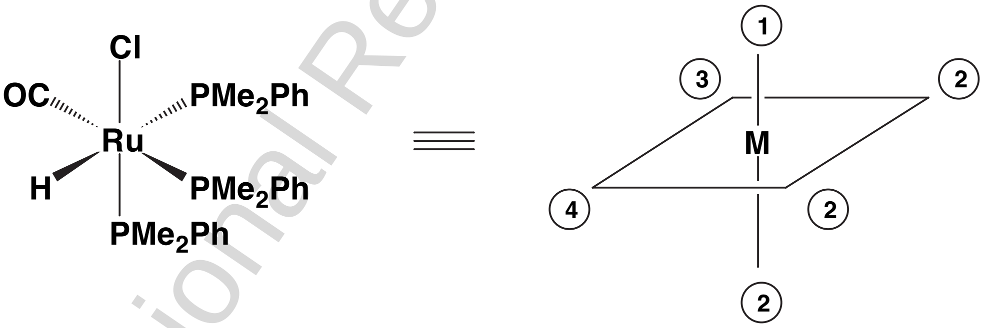
4.



Example 5 shows the complex $[RuCl(CO)H(PMe_2Ph)_3]$ which has the descriptor *OC*-6-24-*A*. The chloride ligand has priority 1.

Example:

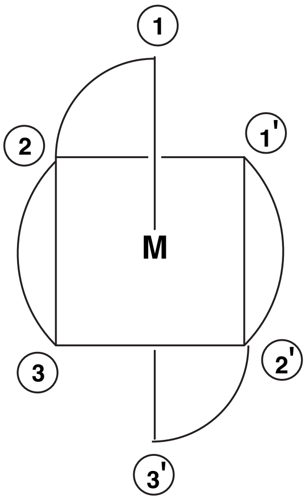
5.



The assignment for polydentate ligands is illustrated by Example 6 which uses the priming convention developed in Section IR-9.3.5. Note that priority number 2 is higher than 2'.

Example:

6.

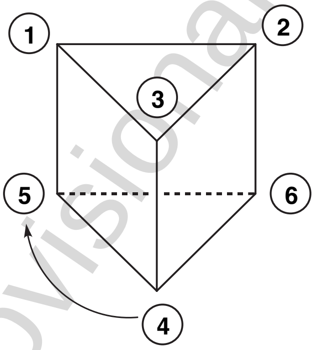


Chirality symbol = *A*

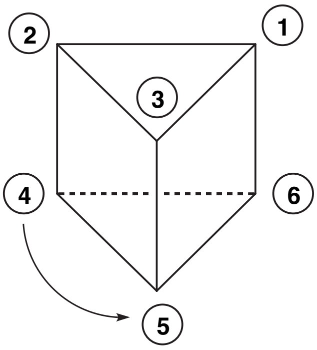
IR-9.3.4.9 *The* C/A *convention for trigonal prismatic centres*

For the trigonal prismatic system, the configuration index is derived from the CIP priority numbers of the ligating atoms opposite the triangular face containing the greater number of ligating atoms of highest CIP priority. The chirality symbol is assigned by viewing the trigonal prism from above the preferred triangular face and noting the direction of progression of the priority sequence for the less preferred triangular face.

Examples:



1. Chirality symbol = *C*



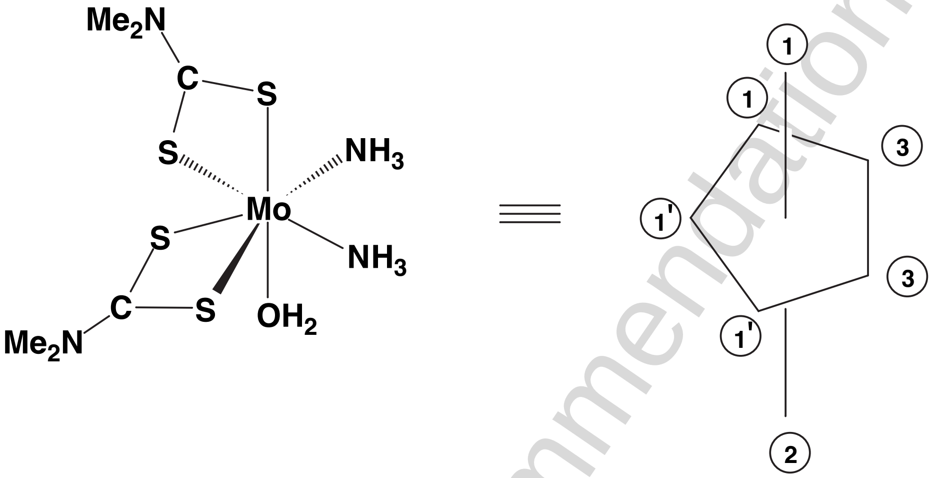
2. Chirality symbol = *A*

IR-9.3.4.10 *The* C/A *convention for other bipyramidal centres*

The procedure used for the trigonal bipyramid is appropriate for other bipyramidal structures. The structure is assigned the symbol *C* or *A*, according to whether the clockwise (*C*) or anticlockwise (*A*) sequence is lower at the first point of difference when the numbers are compared digit by digit from one end to the other (see Sections IR-9.3.4.5 and IR-9.3.4.6) and the molecule is viewed from the higher priority ligand on the reference axis. Example 1 has the descriptor *PBPY*-7-12-11'1'33-*A*.

Example:

1.

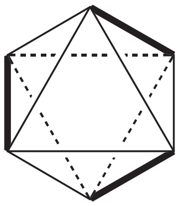


IR-9.3.4.11 *The skew-lines convention*

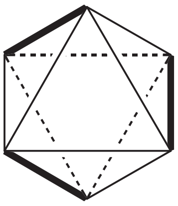
Tris(bidentate) complexes constitute a general family for which a useful unambiguous convention has been developed based on the orientation of skew lines which define a helix.

Examples 1 and 2 represent the *delta* (Δ) and *lambda* (Λ) forms of a complex such as $[Co(NH_2CH_2CH_2NH_2)_3]^{3+}$. The rules define the chiralities of two additional families of structures. These are the *cis*-bis(bidentate) octahedral structures and the conformations of certain chelate rings. It is possible to use the system described below for complexes of higher polydentate ligands, but additional rules are required.[16]

Examples:

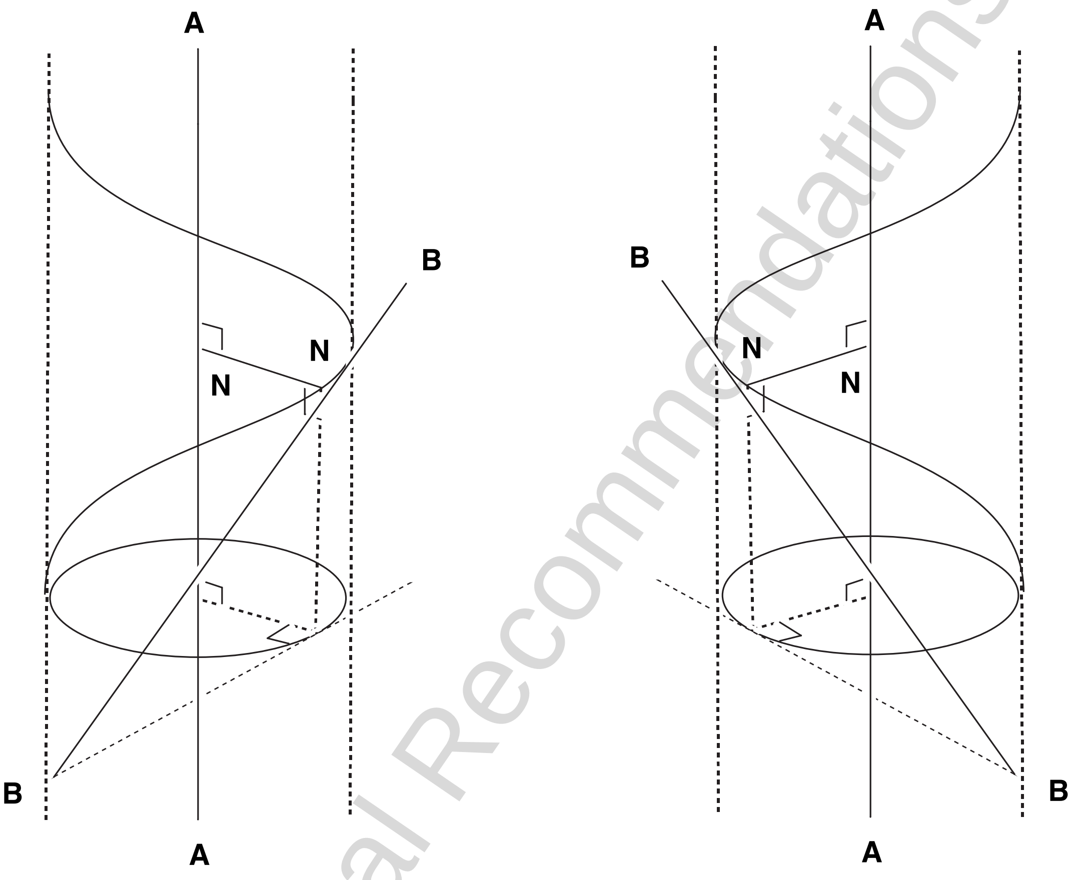


1. *delta* (Δ)



2. *lambda* (Λ)

Two skew-lines which are not orthogonal possess the property of having one, and only one, normal in common. They define a helical system, as illustrated in Figures IR-9.1 and IR-9.2 (below). In Figure IR-9.1, one of the skew-lines, AA, determines the axis of a helix upon a cylinder whose radius is equal to the length of the common normal, NN, to the two skew-lines, AA and BB. The other of the skew-lines, BB, is a tangent to the helix at N and determines the pitch of the helix. In Figure IR-9.2, the two skew-lines AA and BB are seen in projection onto a plane orthogonal to their common normal.



(a) Δ or δ **(b) Λ or λ**

Figure IR-9.1. Two skew lines AA and BB which are not orthogonal define a helical system. In the Figure, AA is taken as the axis of a cylinder whose radius is determined by the common normal NN of the two skew-lines. The line BB is a tangent to the above cylinder at its crossing point with NN and defines a helix upon this cylinder. (a) and (b) illustrate a right- and left-handed helix respectively.

(a) Δ or δ (b) Λ or λ

Figure IR-9.2. The figure shows pairs of non-orthogonal skew-lines in projection upon a plane parallel to both lines. The full line BB is above the plane of the paper, the dotted line AA is below this plane. Case (a) corresponds to (a) of Figure IR-9.1 and defines a right-handed helix. Case (b) corresponds to (b) of Figure IR-9.1 and defines a left-handed helix.

Parts (a) of Figures IR-9.1 and IR-9.2 illustrate a right-handed helix to be associated with the Greek letter delta (Δ referring to configuration, δ to conformation). Parts (b) of Figures IR-9.1 and IR-9.2 illustrate a left-handed helix to be associated with the Greek letter lambda (Λ for configuration, λ for conformation). In view of the symmetry of the representation constituted by two skew-lines, the helix which the first line, say BB, determines around the second, AA, has the same chirality as that which AA determines around BB. As one of the lines is rotated about NN with respect to the other, inversion occurs when the lines are parallel or perpendicular (Figure IR-9.1).

IR-9.3.4.12 *Application of the skew-lines convention to tris(bidentate) octahedral complexes*

Any two of the three chelate rings may be chosen to designate the configuration of tris(bidentate) coordination compounds. The donor atoms of each chelate ring define a line. Two such lines for a pair of chelate rings in the same complex define a helix, one line being the axis of the helix and the other a tangent of the helix at the normal common to the skew-lines. The tangent describes a right-handed (Δ) or a left-handed (Λ) helix with respect to the axis and thereby defines the chirality of that configuration.

IR-9.3.4.13 *Application of the skew-lines convention to bis(bidentate) octahedral complexes*

Figure IR-9.3(a) shows a common orientation of an octahedral tris(bidentate) structure projected onto a plane orthogonal to the three-fold axis of the structure. Figure IR-9.3(b) shows the same structure oriented to emphasize the skew-line relationship between a pair of chelate rings that can be used to define chirality. Figure IR-9.3(c) shows that the same convention can be used for the *cis*-bis(bidentate) complex *cis*-[M(aa)$_2$b$_2$]. The two chelate rings define the two skew-lines that, in turn, define the helix and the chirality of the substance. The procedure is precisely the same as that described for the tris(bidentate) case, but only a single pair of chelate rings is available.

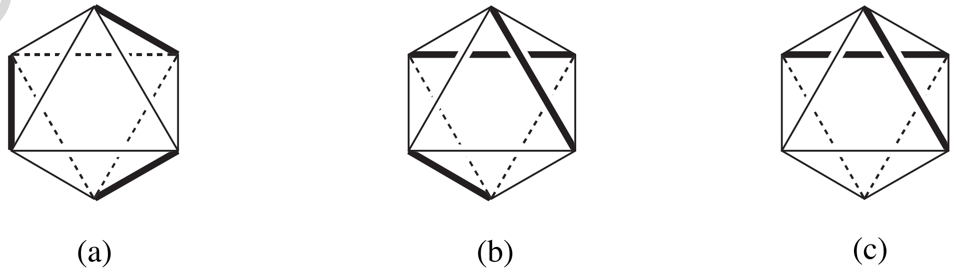
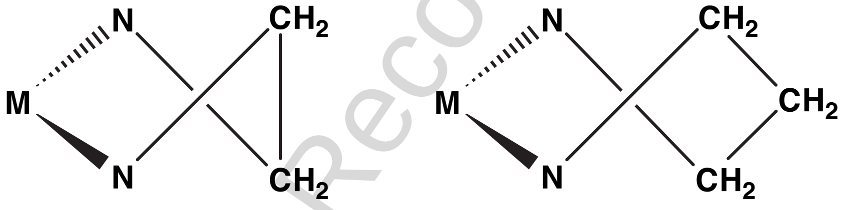


Figure IR-9.3. Two orientations of a tris(bidentate) structure, (a) and (b), to show the chiral relationship between these two species and bis(bidentate) structure (c).

IR-9.3.4.14 *Application of the skew-lines convention to conformations of chelate rings*

In order to assign the chirality of a ring conformation, the line AA in Figure IR-9.2 is defined as that line joining the two ligating atoms of the chelate ring. The other line BB is that joining the two ring atoms which are neighbours to each of the ligating atoms. These two skew-lines define a helix in the usual way. The tangent describes a right-handed (δ) or a left-handed (λ) helix with respect to the axis and thereby defines the conformation in terms of the convention given in Figure IR-9.1. Non-helical situations may also give rise to chirality when the chemical identities of the atoms are considered. For example, the chair and boat conformations of six-membered chelate rings are not chiral. However, if the two donor atoms are not identical then the chelate ring is chiral. Clearly the principles expounded in Section IR-9.3.4.11 do not apply to such cases. The relationship between the convention of Figure IR-9.2 and the usual representation of chelate ring conformation may be seen by comparing Figures IR-9.2 and IR-9.4.



(a) (b)

Figure IR-9.4. δ-Conformation chelate rings: (a) five-membered; (b) six-membered.

IR-9.3.5 Determining ligand priority

IR-9.3.5.1 *General*

The methods for differentiating between stereoisomers outlined earlier in this chapter require the assignment of priorities for the ligands attached to the central atom. These priority numbers are then used in the configuration index, which describes the relative positions of the ligands, and in the assignment of the absolute configuration of the compound.

The following sections outline the method used to arrive at the priority numbers for a given set of ligands (or donor atoms), and the ways that the basic rules have to be modified in order to describe adequately systems that include polydentate ligands. These modifications, which are collectively referred to as the priming convention, make use of primes on the priority numbers to indicate which donor atoms atoms are grouped together within a particular polydentate ligand.

IR-9.3.5.2 *Priority numbers*

The procedure for assigning priorities in mononuclear coordination systems is based on the standard sequence rules developed for enantiomeric carbon compounds by Cahn, Ingold and Prelog.[14] (See also Section P-91 of Ref. 1). These CIP rules can be used quite generally for assigning priorities to groups attached to a central atom.

The essence of these rules, when applied to coordination compounds, is that the ligands attached to the central atom are compared to one another, beginning with the donor atom and then moving outwards in the structure. The comparison is made on the basis of atomic number and then, if required (*e.g.* when isotopes are being specified), atomic mass. Other properties may be used for subsequent comparisons, but the need for them is sufficiently rare that they need not be detailed here.

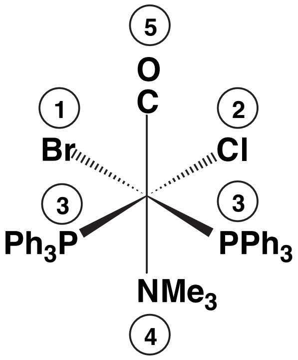
Once the ligands have been compared, the priority numbers are assigned as follows:

(i) identical ligands are assigned the same rank,

(ii) the ligand(s) with highest priority is(are) assigned the priority number 1;
those with the next highest priority, 2; and so on.

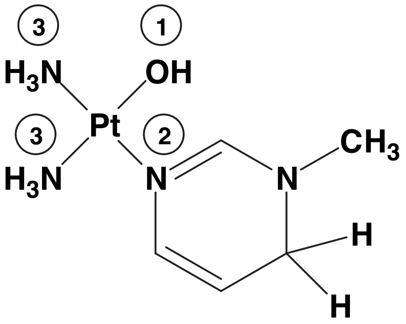
Examples:

1.



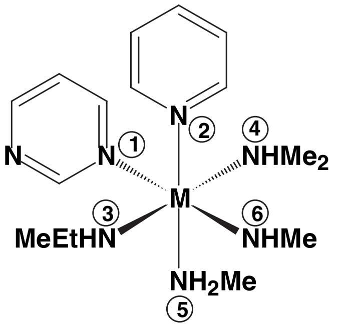
Priority sequence: Br > Cl > PPh_3, PPh_3 > NMe_3 > CO
Priority numbers sequence: 1 > 2 > 3, 3 > 4 > 5

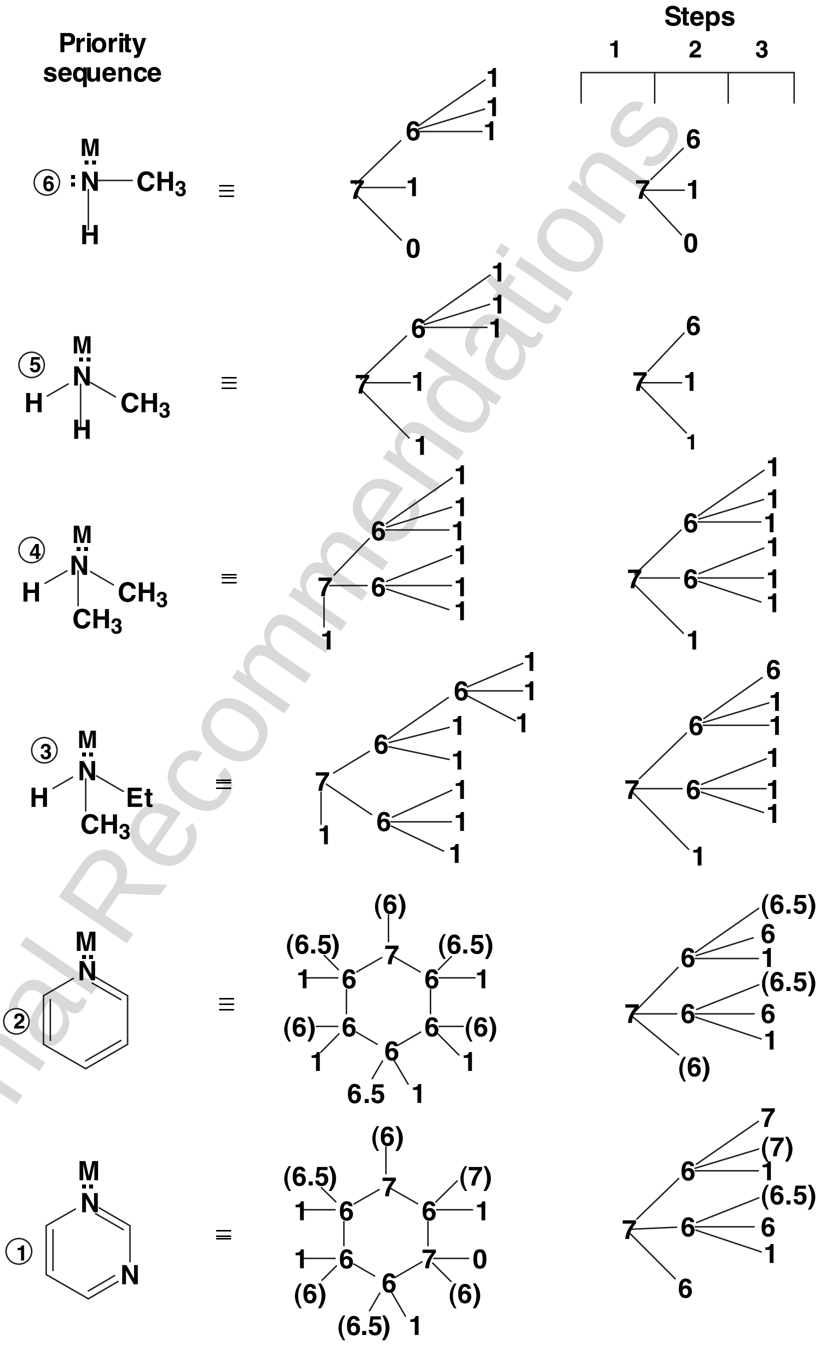
2.



In Example 2, the heterocyclic ligand is given priority 2 since it has a lower atomic number donor than OH, and the substitution of the nitrogen donor ranks it above the ammine ligands.

3.



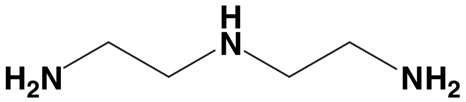


In Example 3, all the ligating atoms are nitrogen atoms. The key illustrates how proceeding along the branches of the ligand constituents allows priorities to be assigned. The numbers in columns 1, 2 and 3 on the right are the atomic numbers of the atoms in the structures, with those in brackets being used to take account of the presence of multiple bonds. The averaging techniques used in the case of resonance structures (last two ligands in the list) are given in the original paper.[14]

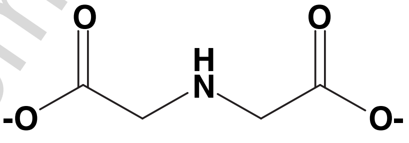
IR-9.3.5.3 *Priming convention*

The priming convention is required in order to avoid ambiguity when using the configuration index to describe the stereochemistry of systems that contain either more than one polydentate ligand of a particular kind, or a polydentate ligand that contains more than one coordinating fragment of a particular kind. This situation is found commonly with bis(tridentate) complexes, but also arises in more complicated cases. The need for this convention is best illustrated by example.

Bis(tridentate) complexes (*i.e.* octahedral complexes containing two identical linear tridentate ligands) may exist in three stereoisomeric forms, and there will be more if the tridentate ligands do not themselves contain some symmetry elements. The three isomers of the simplest case are represented below (Examples 1, 2 and 3), along with their polyhedral symbols (Section IR-9.3.2.1) and configuration indexes (Section IR-9.3.3.4). Complexes of *N*-(2-aminoethyl)ethane-1,2-diamine or iminodiacetate can be described by these diagrams.



N-(2-aminoethyl)ethane-1,2-diamine, or
N,*N*''-ethane-1,2-diylbis(ethane-1,2-diamine)

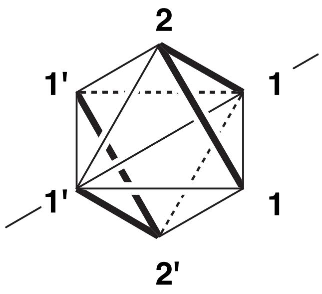


iminodiacetate, or
2,2'-azanediyldiacetate

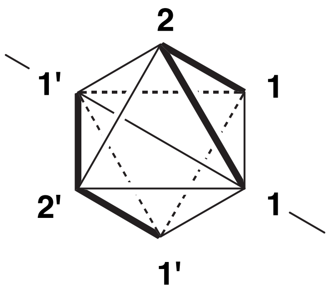
The need for the priming convention can be seen by considering what the configuration indexes of Examples 1 and 3 would be in the absence of the priming convention. The two ligands are identical and consist of two similar fragments fused together. If the primes are ignored, the two complexes have the same distributions of ligating atoms (four donors of priority 1 in a square plane, and two of priority 2 *trans* to one another). They would therefore have the same configuration index, even though they are clearly different complexes.

One way to highlight the difference between these two examples is to note that, in Example 1, all the donor atoms are *trans* to donors that are part of the other ligand. This is not true in Example 3. Using primes to indicate the groupings of donor atoms in particular ligands allows these two stereoisomers to be distinguished from one another by their configuration indexes.

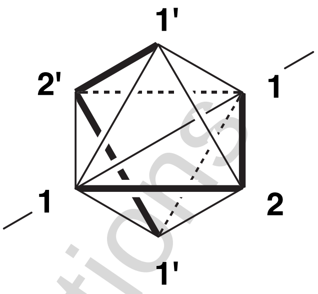
Examples:



1. *OC*-6-1'1'



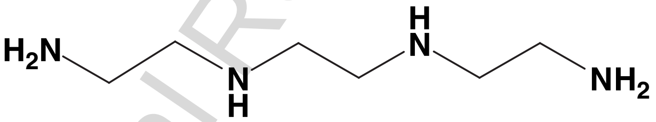
2. *OC*-6-2'1'



3. *OC*-6-11'

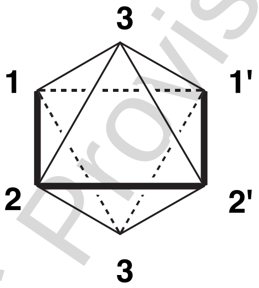
The priority numbers on one of the ligands are arbitrarily primed. The primed number is assigned lower priority than the corresponding unprimed number, but a higher priority than the next higher unprimed number. Thus 1' has lower priority than 1, but higher than 2.

The technique also distinguishes between stereoisomers for complexes of higher polydentate ligands as indicated in Examples 4, 5 and 6 for linear tetradentate ligands such as *N,N'*-bis(2-aminoethyl)ethane-1,2-diamine. In this case, the donor atom priority numbers in half of the tetradentate ligand have been primed.

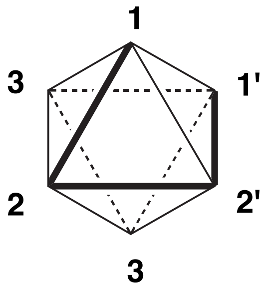


N,*N'*-bis(2-aminoethyl)ethane-1,2-diamine

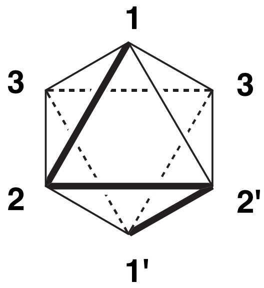
Examples:



4. *OC*-6-2'2



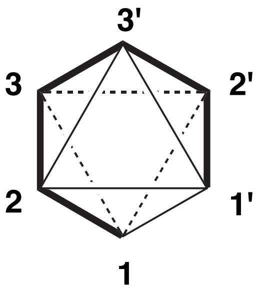
5. *OC*-6-32



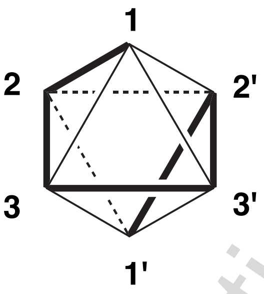
6. *OC*-6-1'3

Pentadentate and hexadentate ligands can be treated similarly, as shown in Examples 7 to 10. Examples 7 and 8 apply to stereoisomers of classic linear hexadentate ligands, whereas Examples 9 and 10 apply to ligands containing a branched structure.

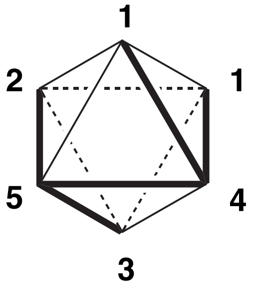
Examples:



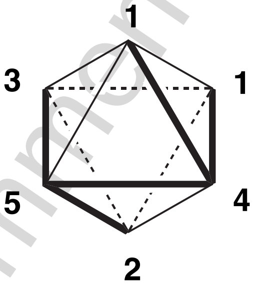
7. *OC*-6-3'3



8. *OC*-6-1'3'



9. *OC*-6-53

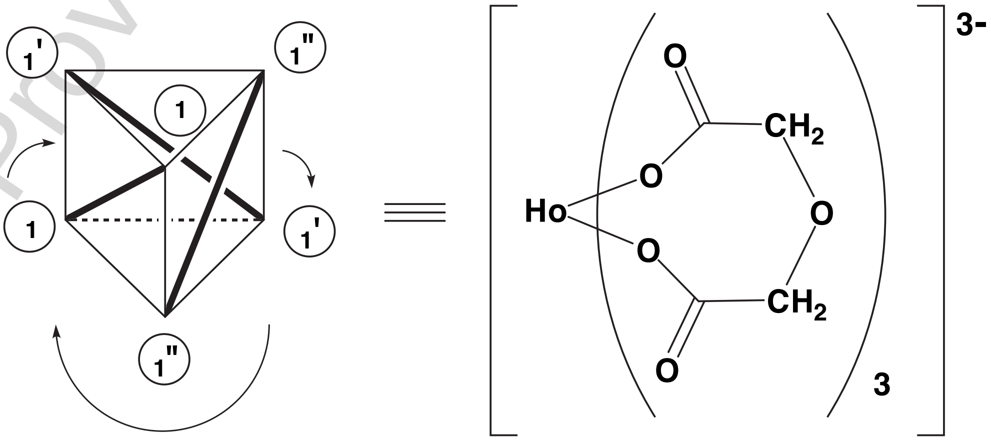


10. *OC*-6-52

Example 11 illustrates the use of priming for assigning absolute configuration in a non-octahedral structure. The chirality designation is determined by the system of assigning primes to ligands. Specifically, the symbol on the top face is placed above the symbol 1" on the bottom face. This produces the sequence shown and the chirality symbol *C*. The stereochemical descriptor is *TPR*-6-1"11'-*C*.

Example:

11.



IR-9.4 FINAL REMARKS

This chapter has described the means by which coordination compounds can be named and formulated. These processes involve firstly identifying the central atom(s) and ligands (by name, formula or abbreviation, depending on the context), and secondly defining the nature of the attachment between the central atom(s) and the ligands. This latter step requires that the coordinating atoms in the ligand be identified (if there is any ambiguity), and that the spatial relationships between the ligands be described.

IR-9.5 REFERENCES

1. **New Blue Book.**
2. In *Nomenclature of Inorganic Chemistry, Recommendations 1990*, Blackwell Scientific Publications, Oxford, 1990, the term didentate was used rather than bidentate, for reasons of linguistic consistency. Reversion to the previously accepted term, bidentate, reflects common usage.
3. For consistency, halide ligands are named fluorido, chlorido, bromido and iodido throughout this book. Similarly, coordinated cyanide is named cyanido. The names chloro, cyano, *etc*. are alternatives.
4. The names of the other hydrogen isotopes are discussed in Section IR-3.3.2.
5. The names of organic ligands should be assigned in accordance with IUPAC recommendations, see Ref. 1.
6. In order to simplify the rules and to resolve ambiguities that may arise when it is not clear whether a ligand is charged or not, the charge on a ligand is no longer considered in determining ligand order in the formulae of coordination compounds. (In *Nomenclature of Inorganic Chemistry, Recommendations 1990*, Blackwell Scientific Publications, Oxford, 1990, anionic ligands were listed before neutral ligands).
7. Chapter II-7 of *Nomenclature of Inorganic Chemistry II, Recommendations 2000*, Royal Society of Chemistry, 2001.
8. J. B. Casey, W.J. Evans and W.H. Powell, *Inorg. Chem*., **20**, 1333 (1981).
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16. M. Brorson, T. Damhus and C.E. Schaeffer, *Inorg. Chem.*, **22**, 1569 (1983).