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Prepared for publication by Neil G Connelly, Ture Damhus Richard M Hartshorn, Alan T Hutton

Nomenclature of Inorganic Chemistry

IUPAC Recommendations 2005





















Nomenclature of Inorganic Chemistry IUPAC RECOMMENDATIONS 2005

Issued by the Division of Chemical Nomenclature and Structure Representation in collaboration with the Division of Inorganic Chemistry

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NOMENCLATURE OF INORGANIC CHEMISTRY IUPAC Recommendations 2005

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Preface

Chemical nomenclature must evolve to reflect the needs of the community that makes use of it. In particular, nomenclature must be created to describe new compounds or classes of compounds; modified to resolve ambiguities which might arise; or clarified where there is confusion over the way in which nomenclature should be used. There is also a need to make nomenclature as systematic and uncomplicated as possible in order to assist less familiar users (for example, because they are only in the process of studying chemistry or are non-chemists who need to deal with chemicals at work or at home). A revision of *Nomenclature of Inorganic Chemistry, IUPAC Recommendations 1990* (Red Book I) was therefore initiated in 1998, under the guidance of the IUPAC Commission on Nomenclature of Inorganic Chemistry (CNIC) and then, on the abolition of CNIC in 2001 as part of the general restructuring of IUPAC, by a project group working under the auspices of the Division of Chemical Nomenclature and Structure Representation (Division VIII).

The need to ensure that inorganic and organic nomenclature systems are, as far as possible, consistent has resulted in extensive cooperation between the editors of the revised Red Book and the editors of *Nomenclature of Organic Chemistry, IUPAC Recommendations* (the revised 'Blue Book', in preparation). At present, the concept of preferred IUPAC names (PINs), an important element in the revision of the Blue Book, has not been extended to inorganic nomenclature (though preferred names are used herein for organic, *i.e.* carbon-containing, compounds when appropriate). A planned future project on inorganic PINs will need to face the problem of choice between the equally valid nomenclature systems currently in use.

The present book supersedes not only Red Book I but also, where appropriate, Nomenclature of Inorganic Chemistry II, IUPAC Recommendations 2000 (Red Book II). One of the main changes from Red Book I is the different organization of material, adopted to improve clarity. Thus, Chapters IR-5 (Compositional Nomenclature, and Overview of Names of Ions and Radicals), IR-6 (Parent Hydride Names and Substitutive Nomenclature), and IR-7 (Additive Nomenclature) deal with the general characteristics of the three main nomenclature systems applied to inorganic compounds. (Note that the notation 'IR-' is used to distinguish chapters and sections in the current book from those in Red Book I, prefixed 'I-'). The next three chapters deal with their application, particularly that of additive nomenclature, to three large classes of compounds: inorganic acids and derivatives (Chapter IR-8), coordination compounds (Chapter IR-9) and organometallic compounds (Chapter IR-10). Overall, the emphasis on additive nomenclature (generalized from the classical nomenclature of coordination compounds) which was already apparent in Red Book I is reinforced here. Examples are even included of organic compounds, from the borderline between inorganic and organic chemistry, which may be conveniently named using additive nomenclature (although their PINs will be different).

One important addition in this book is Chapter IR-10 on Organometallic Compounds. The separation of this material from that on Coordination Compounds (Chapter IR-9) reflects the huge growth in importance of organometallic chemistry and the very different

problems associated with the presence of π -bonded ligands. Chapter IR-9 is also considerably changed (cf. Red Book I, Chapter I-10). This revised chapter includes a clarification of the use of the η and κ conventions in coordination and organometallic compounds (Section IR-9.2.4.3); new rules for the ordering of central atoms in names of polynuclear compounds (Section IR-9.2.5.6); the bringing together of sections on configuration (Section IR-9.3) and their separation from those on constitution (Section IR-9.2); and the addition of polyhedral symbols for T-shaped (Section IR-9.3.3.7) and seesaw (Section IR-9.3.3.8) molecules, along with guidance on how to choose between these shapes and those of closely related structures (Section IR-9.3.2.2).

The chapter on Oxoacids and Derived Anions (Red Book I, Chapter I-9) has also been extensively modified. Now called Inorganic Acids and Derivatives (Chapter IR-8), it includes the slightly revised concept of 'hydrogen names' in Section IR-8.4 (and some traditional 'ous' and 'ic' names have been reinstated for consistency and because they are required for organic nomenclature purposes, *i.e.* in the new Blue Book).

The reader facing the problem of how to name a given compound or species may find help in several ways. A flowchart is provided in Section IR-1.5.3.5 which will in most cases guide the user to a Section or Chapter where rules can be found for generating at least one possible name; a second flowchart is given in Section IR-9.2.1 to assist in the application of additive nomenclature specifically to coordination and organometallic compounds. A more detailed subject index is also provided, as is an extended guide to possible alternative names of a wide range of simple inorganic compounds, ions and radicals (in Table IX).

For most compounds, formulae are another important type of compositional or structural representation and for some compounds a formula is perhaps easier to construct. In Chapter IR-4 (Formulae) several changes are made in order to make the presentation of a formula and its corresponding name more consistent, e.g. the order of ligand citation (which does not now depend on the charge on the ligand) (Section IR-4.4.3.2) and the order and use of enclosing marks (simplified and more consistent with the usage proposed for the nomenclature of organic compounds) (Section IR-4.2.3). In addition, the use of ligand abbreviations can make formulae less cumbersome. Thus, recommendations for the construction and use of abbreviations are provided in Section IR-4.4.4, with an extensive list of established abbreviations given in Table VII (and with structural formulae for the ligands given in Table VIII).

Two chapters of Red Book I have been shortened or subsumed since in both areas extensive revision is still necessary. First, the chapter on Solids (IR-11) now describes only basic topics, more recent developments in this area tending to be covered by publications from the International Union of Crystallography (IUCr). It is to be hoped that future cooperation between IUPAC and IUCr will lead to the additional nomenclature required for the rapidly expanding field of solid-state chemistry.

Second, boron chemistry, particularly that of polynuclear compounds, has also seen extensive development. Again, therefore, only the basics of the nomenclature of boron-containing compounds are covered here (*cf.* the separate, more comprehensive but dated, chapter on boron nomenclature, I-11, in Red Book I), within Chapter IR-6 (Parent Hydride Names and Substitutive Nomenclature), while more advanced aspects are left for elaboration in a future project.

Other changes include a section on new elements and the procedure by which they are now named (Section IR-3.1) and a simplified coverage of the systematic method for naming

chains and rings (adapted from Chapter II-5 of Red Book II). Lesser omissions include the section on single strand polymers (now updated as Chapter II-7 in Red Book II) and the several different outdated versions of the periodic table. (That on the inside front cover is the current IUPAC-agreed version.)

Some new recommendations represent breaks with tradition, in the interest of increased clarity and consistency. For example, the application of the ending 'ido' to all anionic ligands with 'ide' names in additive nomenclature (e.g. chlorido and cyanido instead of chloro and cyano, and hydrido throughout, i.e. no exception in boron nomenclature) is part of a general move to a more systematic approach.

Acknowledgements

It is important to remember that the current volume has evolved from past versions of the Red Book and it is therefore appropriate first to acknowledge the efforts of previous editors and contributors. However, we would also like to thank the many people without whose help this revision would not have come to fruition. Members of CNIC were involved in the early stages of the revision (including Stanley Kirschner who began the task of compiling ligand abbreviations and what has become Tables VII and VIII), and members of the IUPAC Division VIII Advisory Subcommittee (particularly Jonathan Brecher, Piroska Fodor-Csányi, Risto Laitinen, Jeff Leigh and Alan McNaught) and the editors of the revised Blue Book (Warren Powell and Henri Favre) have made extremely valuable comments. However, the bulk of the work has been carried out by a project group comprising the two Senior Editors, Richard Hartshorn and Alan Hutton.

NEIL G. CONNELLY and TURE DAMHUS (Senior Editors)

Contents

IR-1	GENERAL AIMS, FUNCTIONS AND METHODS OF CHEMICAL NOMENCLATURE 1
IR-1.1	Introduction 1
IR-1.2	History of chemical nomenclature 2
IR-1.3	Aims of chemical nomenclature 3
IR-1.4	Functions of chemical nomenclature 4
IR-1.5	Methods of inorganic nomenclature 4
IR-1.6	Changes to previous IUPAC recommendations 8
IR-1.7	Nomenclature recommendations in other areas of chemistry 13
IR-1.8	References 13
IR-2	GRAMMAR 15
IR-2.1	Introduction 16
IR-2.2	Enclosing marks 17
IR-2.3	Hyphens, plus and minus signs, 'em' dashes and bond indicators 24
IR-2.4	Solidus 27
IR-2.5	Dots, colons, commas and semicolons 27
IR-2.6	Spaces 30
IR-2.7	Elisions 31
IR-2.8	Numerals 31
IR-2.9	Italic letters 34
IR-2.10	Greek alphabet 35
IR-2.11	Asterisks 36
IR-2.12	Primes 36
IR-2.13	Multiplicative prefixes 37
IR-2.14	Locants 38
IR-2.15	Ordering principles 40
IR-2.16	Final remarks 44
IR-2.17	References 45
IR-3	ELEMENTS 46
IR-3.1	Names and symbols of atoms 46
IR-3.2	Indication of mass, charge and atomic number using indexes (subscript and superscripts) 47

CONTENTS

IR-3.3	Isotopes 48
IR-3.4	Elements (or elementary substances) 48
IR-3.5	Elements in the periodic table 51
IR-3.6	References 52
IR-4	FORMULAE 53
IR-4.1	Introduction 54
IR-4.2	Definitions of types of formula 54
IR-4.3	Indication of ionic charge 57
IR-4.4	Sequence of citation of symbols in formulae 58
IR-4.5	Isotopically modified compounds 64
IR-4.6	Optional modifiers of formulae 65
IR-4.7	References 67
IR-5	COMPOSITIONAL NOMENCLATURE, AND OVERVIEW OF NAMES OF IONS AND RADICALS 68
IR-5.1	Introduction 68
IR-5.2	Stoichiometric names of elements and binary compounds 69
IR-5.3	Names of ions and radicals 70
IR-5.4	Generalized stoichiometric names 75
IR-5.5	Names of (formal) addition compounds 80
IR-5.6	Summary 81
IR-5.7	References 82
IR-6	PARENT HYDRIDE NAMES AND SUBSTITUTIVE NOMENCLATURE 83
IR-6.1	Introduction 84
IR-6.2	Parent hydride names 84
IR-6.3	Substitutive names of derivatives of parent hydrides 101
IR-6.4	Names of ions and radicals derived from parent hydrides 105
IR-6.5	References 110
IR-7	ADDITIVE NOMENCLATURE 111
IR-7.1	Introduction 111
IR-7.2	Mononuclear entities 113
IR-7.3	Polynuclear entities 114
IR-7.4	Inorganic chains and rings 118
IR-7.5	References 123

IR-8	INORGANIC ACIDS AND DERIVATIVES 124
IR-8.1	Introduction and overview 124
IR-8.2	General principles for systematic naming of acids 126
IR-8.3	Additive names 133
IR-8.4	Hydrogen names 134
IR-8.5	Abbreviated hydrogen names for certain anions 137
IR-8.6	Functional replacement names for derivatives of oxoacids 137
IR-8.7	References 141
IR-9	COORDINATION COMPOUNDS 142
IR-9.1	Introduction 144
IR-9.2	Describing the constitution of coordination compounds 149
IR-9.3	Describing the configuration of coordination entities 174
IR-9.4	Final remarks 198
IR-9.5	References 198
IR-10	ORGANOMETALLIC COMPOUNDS 200
IR-10.1	Introduction 200
IR-10.2	Nomenclature of organometallic compounds of the transition elements 201
IR-10.3	Nomenclature of organometallic compounds of the main group elements 228
IR-10.4	Ordering of central atoms in polynuclear organometallic compounds 232
IR-10.5	References 233
IR-11	SOLIDS 235
IR-11.1	Introduction 236
IR-11.2	Names of solid phases 236
IR-11.3	Chemical composition 237
IR-11.4	Point defect (Kröger-Vink) notation 238
IR-11.5	Phase nomenclature 241
IR-11.6	Non-stoichiometric phases 242
IR-11.7	Polymorphism 245
IR-11.8	Final remarks 246
IR-11.9	References 246

CONTENTS

TABLES

Table I	Names, symbols and atomic numbers of the elements 248
Table II	Temporary names and symbols for elements of atomic number greater than 111 250
Table III	Suffixes and endings 251
Table IV	Multiplicative prefixes 258
Table V	Geometrical and structural affixes 259
Table VI	Element sequence 260
Table VII	Ligand abbreviations 261
Table VIII	Structural formulae of selected ligands 269
Table IX	Names of homoatomic, binary and certain other simple molecules, ions, compounds, radicals and substituent groups 280
Table X	Anion names, 'a' terms used in substitutive nomenclature and 'y' terms used in chains and rings nomenclature 337

SUBJECT INDEX 341

IR-1 General Aims, Functions and Methods of Chemical Nomenclature

CONTENTS

- IR-1.1 Introduction
- IR-1.2 History of chemical nomenclature
 - IR-1.2.1 International cooperation on inorganic nomenclature
- IR-1.3 Aims of chemical nomenclature
- IR-1.4 Functions of chemical nomenclature
- IR-1.5 Methods of inorganic nomenclature
 - IR-1.5.1 Formulation of rules
 - IR-1.5.2 Name construction
 - IR-1.5.3 Systems of nomenclature
 - IR-1.5.3.1 General
 - IR-1.5.3.2 Compositional nomenclature
 - IR-1.5.3.3 Substitutive nomenclature
 - IR-1.5.3.4 Additive nomenclature
 - IR-1.5.3.5 General naming procedures
- IR-1.6 Changes to previous IUPAC recommendations
 - IR-1.6.1 Names of cations
 - IR-1.6.2 Names of anions
 - IR-1.6.3 The element sequence of Table VI
 - IR-1.6.4 Names of anionic ligands in (formal) coordination entities
 - IR-1.6.5 Formulae for (formal) coordination entities
 - IR-1.6.6 Additive names of polynuclear entities
 - IR-1.6.7 Names of inorganic acids
 - IR-1.6.8 Addition compounds
 - IR-1.6.9 Miscellaneous
- IR-1.7 Nomenclature recommendations in other areas of chemistry
- IR-1.8 References

IR-1.1 INTRODUCTION

This Chapter provides a brief historical overview of chemical nomenclature (Section IR-1.2) followed by summaries of its aims, functions and methods (Sections IR-1.3 to IR-1.5). There are several systems of nomenclature that can be applied to inorganic compounds, briefly described in Section IR-1.5.3.5 as an introduction to the later, more detailed, chapters. Because each system can provide a valid name for a compound, a flowchart is presented in Section IR-1.5.3 which should help identify which is the most appropriate for the type of compound of interest. Section IR-1.6 summarises the major changes from previous

recommendations and, finally, reference is made in Section IR-1.7 to nomenclature in other areas of chemistry, underlining that inorganic chemistry is part of an integrated whole.

IR-1.2 HISTORY OF CHEMICAL NOMENCLATURE

The activities of alchemy and of the technical arts practised prior to the founding of what we now know as the science of chemistry produced a rich vocabulary for describing chemical substances although the names for individual species gave little indication of composition. However, almost as soon as the true science of chemistry was established a 'system' of chemical nomenclature was developed by Guyton de Morveau in 1782. Guyton's statement of the need for a 'constant method of denomination, which helps the intelligence and relieves the memory' clearly defines the basic aims of chemical nomenclature. His system was extended by a joint contribution² with Lavoisier, Berthollet, and de Fourcroy and was popularized by Lavoisier. Later, Berzelius championed Lavoisier's ideas, adapting the nomenclature to the Germanic languages, expanding the system and adding many new terms. This system, formulated before the enunciation of the atomic theory by Dalton, was based upon the concept of elements forming compounds with oxygen, the oxides in turn reacting with each other to form salts; the two-word names in some ways resembled the binary system introduced by Linnaeus (Carl von Linné) for plant and animal species.

When atomic theory developed to the point where it was possible to write specific formulae for the various oxides and other binary compounds, names reflecting composition more or less accurately then became common; no names reflecting the composition of the oxosalts were ever adopted, however. As the number of inorganic compounds rapidly grew, the essential pattern of nomenclature was little altered until near the end of the 19th century. As a need arose, a name was proposed and nomenclature grew by accretion rather than by systematization.

When Arrhenius focused attention on ions as well as molecules, it became necessary to name charged particles in addition to neutral species. It was not deemed necessary to develop a new nomenclature for salts; cations were designated by the names of the appropriate metal and anions by a modified name of the non-metal portion.

Along with the theory of coordination, Werner proposed⁵ a system of nomenclature for coordination entities which not only reproduced their compositions but also indicated many of their structures. Werner's system was completely additive in that the names of the ligands were cited, followed by the name of the central atom (modified by the ending 'ate' if the complex was an anion). Werner also used structural descriptors and locants. The additive nomenclature system was capable of expansion and adaptation to new compounds and even to other fields of chemistry.

IR-1.2.1 International cooperation on inorganic nomenclature

In 1892 a conference in Geneva⁶ laid the basis for an internationally accepted system of organic nomenclature but at that time there was nothing comparable for inorganic nomenclature. Thus, many *ad hoc* systems had developed for particular rather than general purposes, and two or more methods often evolved for naming a given compound belonging

to a given class. Each name might have value in a specific situation, or be preferred by some users, but there was then the possibility of confusion.

The need for uniform practice among English-speaking chemists was recognized as early as 1886 and resulted in agreements on usage by the British and American Chemical Societies. In 1913, the Council of the International Association of Chemical Societies appointed a commission of inorganic and organic nomenclature, but World War I abruptly ended its activities. Work was resumed in 1921 when IUPAC, at its second conference, appointed commissions on the nomenclature of inorganic, organic, and biological chemistry.

The first comprehensive report of the inorganic commission, in 1940,⁷ had a major effect on the systematization of inorganic nomenclature and made many chemists aware of the necessity for developing a more fully systematic nomenclature. Among the significant features of this initial report were the adoption of the Stock system for indicating oxidation states, the establishment of orders for citing constituents of binary compounds in formulae and in names, the discouragement of the use of bicarbonate, *etc.* in the names of acid salts, and the development of uniform practices for naming addition compounds.

These IUPAC recommendations were then revised and issued as a small book in 1959⁸ followed by a second revision in 1971⁹ and a supplement, entitled *How to Name an Inorganic Substance*, in 1977.¹⁰ In 1990 the IUPAC recommendations were again fully revised¹¹ in order to bring together the many and varied changes which had occurred in the previous 20 years.

More specialized areas have also been considered, concerning polyanions, ¹² metal complexes of tetrapyrroles (based on Ref. 13), inorganic chain and ring compounds, ¹⁴ and graphite intercalation compounds. ¹⁵ These topics, together with revised versions of papers on isotopically modified inorganic compounds, ¹⁶ hydrides of nitrogen and derived cations, anions and ligands, ¹⁷ and regular single-strand and quasi single-strand inorganic and coordination polymers, ¹⁸ comprise the seven chapters of *Nomenclature of Inorganic Chemistry II*, *IUPAC Recommendations 2000*. ¹⁹ A paper entitled *Nomenclature of Organometallic Compounds of the Transition Elements* ²⁰ forms the basis for Chapter IR-10 of this book.

IR-1.3 AIMS OF CHEMICAL NOMENCLATURE

The primary aim of chemical nomenclature is to provide methodology for assigning descriptors (names and formulae) to chemical species so that they can be identified without ambiguity, thereby facilitating communication. A subsidiary aim is to achieve standardization. Although this need not be so absolute as to require only one name for a substance, the number of 'acceptable' names needs to be minimized.

When developing a system of nomenclature, public needs and common usage must also be borne in mind. In some cases, the only requirement may be to identify a substance, essentially the requirement prior to the late 18th century. Thus, local names and abbreviations are still used by small groups of specialists. Such local names suffice as long as the specialists understand the devices used for identification. However, this is not nomenclature as defined above since local names do not necessarily convey structural and compositional information to a wider audience. To be widely useful, a nomenclature system must be recognisable, unambiguous, and general; the unnecessary use of local names and abbreviations in formal scientific language should therefore be discouraged.

IR-1.4 FUNCTIONS OF CHEMICAL NOMENCLATURE

The first level of nomenclature, beyond the assignment of totally trivial names, gives some systematic information about a substance but does not allow the inference of composition. Most of the common names of the oxoacids (e.g. sulfuric acid, perchloric acid) and of their salts are of this type. Such names may be termed semi-systematic and as long as they are used for common materials and understood by chemists, they are acceptable. However, it should be recognized that they may hinder compositional understanding by those with limited chemical training.

When a name itself allows the inference of the stoichiometric formula of a compound according to general rules, it becomes truly systematic. Only a name at this second level of nomenclature becomes suitable for retrieval purposes.

The desire to incorporate information concerning the three-dimensional structures of substances has grown rapidly and the systematization of nomenclature has therefore had to expand to a third level of sophistication. Few chemists want to use such a degree of sophistication every time they refer to a compound, but they may wish to do so when appropriate.

A fourth level of nomenclature may be required for the compilation and use of extensive indexes. Because the cost to both compiler and searcher of multiple entries for a given substance may be prohibitive, it becomes necessary to develop systematic hierarchical rules that yield a unique name for a given substance.

IR-1.5 METHODS OF INORGANIC NOMENCLATURE

IR-1.5.1 Formulation of rules

The revision of nomenclature is a continuous process as new discoveries make fresh demands on nomenclature systems. IUPAC, through the Division of Chemical Nomenclature and Structure Representation (formed in 2001), studies all aspects of the nomenclature of inorganic and other substances, recommending the most desirable practices to meet specific problems, for example for writing formulae and generating names. New nomenclature rules need to be formulated precisely, to provide a systematic basis for assigning names and formulae within the defined areas of application. As far as possible, such rules should be consistent with existing recommended nomenclature, in both inorganic and other areas of chemistry, and take into account emerging chemistry.

IR-1.5.2 Name construction

The systematic naming of an inorganic substance involves the construction of a name from entities which are manipulated in accordance with defined procedures to provide compositional and structural information. The element names (or roots derived from them or from their Latin equivalents) (Tables I and II*, see also Chapter IR-3) are combined with affixes in order to construct systematic names by procedures which are called systems of nomenclature.

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

There are several accepted systems for the construction of names, as discussed in Section IR-1.5.3. Perhaps the simplest is that used for naming binary substances. This set of rules leads to a name such as iron dichloride for the substance FeCl₂; this name involves the juxtaposition of element names (iron, chlorine), their ordering in a specific way (electropositive before electronegative), the modification of an element name to indicate charge (the 'ide' ending designates an elementary anion and, more generally, an element being treated formally as an anion), and the use of the multiplicative prefix 'di' to indicate composition.

Whatever the pattern of nomenclature, names are constructed from entities such as:

```
element name roots,
multiplicative prefixes,
prefixes indicating atoms or groups — either substituents or ligands,
suffixes indicating charge,
names and endings denoting parent compounds,
suffixes indicating characteristic substituent groups,
infixes,
locants,
descriptors (structural, geometric, spatial, etc.),
punctuation.
```

IR-1.5.3 Systems of nomenclature

IR-1.5.3.1 General

In the development of nomenclature, several systems have emerged for the construction of chemical names; each system has its own inherent logic and set of rules (grammar). Some systems are broadly applicable whereas practice has led to the use of specialized systems in particular areas of chemistry. The existence of several distinct nomenclature systems leads to logically consistent alternative names for a given substance. Although this flexibility is useful in some contexts, the excessive proliferation of alternatives can hamper communication and even impede trade and legislation procedures. Confusion can also occur when the grammar of one nomenclature system is mistakenly used in another, leading to names that do not represent any given system.

Three systems are of primary importance in inorganic chemistry, namely compositional, substitutive and additive nomenclature; they are described in more detail in Chapters IR-5, IR-6 and IR-7, respectively. Additive nomenclature is perhaps the most generally applicable in inorganic chemistry, but substitutive nomenclature may be applied in appropriate areas. These two systems require knowledge of the constitution (connectivity) of the compound or species being named. If only the stoichiometry or composition of a compound is known or to be communicated, compositional nomenclature is used.

IR-1.5.3.2 Compositional nomenclature

This term is used in the present recommendations to denote name constructions which are based solely on the composition of the substances or species being named, as opposed to