(8) Private communication.
(9) We have chosen not to use polynuclear examples because they would require us to present an ad hoc numbering for coordination centers in polynuclear compounds. Long experience in organic ring nomenclature and boron cluster numbering has indicated to us that great mischief in communication can and will occur when several numbering systems are simultaneously in use. Therefore, despite the temptation to forge our own proposals, prudence requires that this fundamental question should more appropriately be considered a separate issue.
(10) The more systematic index names are tris[2-pyridinecarboxyaldehyde-κN (2-pyridinylmethylene)hydrazone-κN^1]iron(2+) and bis[2-pyridinecarboxaldehyde-κN (2-pyridinyl-κN-methylene)hydrazone-κN^1]iron(2+). By inspection of these systematic index names, it is evident that the kappa infix atomic symbol locant fits even more naturally into the extended multipart ligand names than those based on more traditional nomenclature.
(11) F. A. Cotton, *J. Am. Chem. Soc.*, **90**, 6230 (1968).
(12) "IUPAC, Nomenclature for Inorganic Chemistry (1970)", 2nd ed, Butterworths, London, 1971, Rule 7.42 and Table III, p 103.
(13) Reference 12.
(14) H. Tom Dick and A. Orloppa, *Angew. Chem., Int. Ed. Engl.*, **14**, 251 (1975).
(15) -$\kappa N,\kappa N'$ could also be used to indicate the nitrogen chelation in [*N*,-*N'*-ethanediylidenebis(isopropylamine)].
(16) R. B. King, *J. Organomet. Chem.*, **100**, 111 (1975).
(17) R. B. King and K. N. Chen, *Inorg. Chem.*, **16**, 1164 (1977).
(18) R. St. L. Bruce, M. K. Cooper, and B. G. McGrath, *J. Chem. Soc. D*, **2**, 69 (1970).
(19) -$\kappa N^1,\kappa N^4,\kappa N^7$ could also be used as the ligand locants for diethylenetriamine.
(20) Ado-1-O = adenosine 1-oxide.

Contribution from the Agricultural Research Council, Unit of Nitrogen Fixation, The University of Sussex, Brighton, Sussex, BN1 9QJ, England

The Designation of Coordinating Sites in Ligands

G. JEFFERY LEIGH

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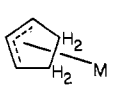
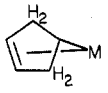
An alternative method to that described in the previous paper for designating coordinating sites in ligands is described. It supersedes the η system but, like it, uses a single designator, Ω. The method is particularly suitable for naming small polynuclear complexes.

Introduction

The problem of the designation of coordinating sites in ligands has been recognized for many years, and specific devices for dealing with it have been suggested by the Commission for the Nomenclature of Inorganic Chemistry of IUPAC (the use of italicized donor-element symbols with appropriate locants and primes)[1,2] and by Cotton (the "*hapto*" or η convention).[3] The use of italicized element symbols is not necessarily adequate when very complex ligands are involved and is incapable of dealing with situations in which more than one metal atom may bind to the same complex ligand. The "*hapto*" convention of Cotton, as adopted by IUPAC,[2] has been used in part more loosely than intended and in some ways more restrictively. For example, it was clearly intended by IUPAC that the convention should apply to sets of contiguous donor atoms of any kind, not just to carbon. The term "*monohapto*" is widely current, though this is a misnomer in IUPAC terms.[2] There is a clear need for a convention to allow the designation of "*monohapto*" coordination and to allow a distinction between (*trihapto*?) situations such as shown in structures a and b.



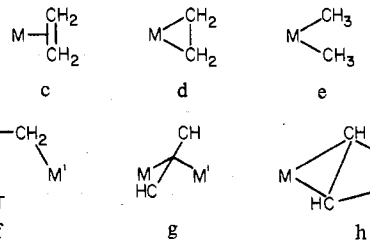
a



b

For this reason Busch and Sloan,[4] extending an idea due to Lozac'h[5] and Gustafson,[6] introduced the κ convention for designating simple coordination sites. The format they propose is sensible but the convention introduces a misleading concept and is limited in its description of multinuclear systems.

It misleads in that it implies a difference in bond type which is designated by η and κ which is not justified. In usage, η is generally understood to imply electron delocalization over several carbon atoms, though whether this really occurs is often a matter of subjective opinion rather than chemical discussion. However, there is no difference in principle between the binding of two carbon atoms to a metal as in structures c, d, or e, or even in f, g, or h. Should structures c and h be



designated by η and structures e and f by κ or is the distinction unnecessary? In short, two symbols are superfluous, and possibly misleading. A single designator is sufficient, and avoids arguments over electron delocalization.[7]

The η/κ symbolism is inadequate in that in polynuclear species it may be necessary to define which ligand atoms are bound to which metals. Neither the η nor the κ convention enables one to do this.

To overcome the above objections, I wish to propose an extension, which I name the Ω convention[8] which is at once both more flexible and more widely applicable than either κ or η, separately or together. The formating procedure closely follows that for κ,[4] upon which it is based.

The Ω Convention

(a) Single Ligand Atoms in Polyatomic Ligands. These are denoted by the italic element symbol of the ligand atom preceded by the Greek letter Ω. This is placed directly after that part of the ligand name in which the ligating group is contained. Any locants, primes, etc., needed to identify the ligand atom uniquely are indicated by superscripts to the italic element symbol. The Ω designator is separated from the conventional part of the name by a hyphen.

(b) More Than One Nonadjacent Single Ligand Atom in Polyatomic Ligands. When there is more than one ligand atom in the ligand, each ligand atom is cited in the name as in (a). Where two ligand atoms are cited in the same part of the name, they are written in the order of Table IV of the IUPAC

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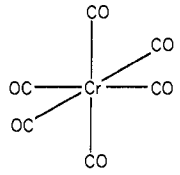
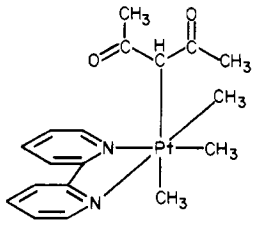
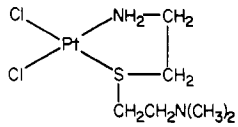


example 1, hexakis(carbonyl-ΩC)chromium

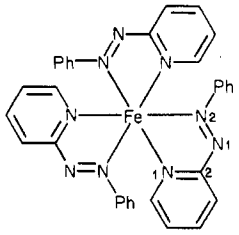
rules[2] (see section 7.513 (b)), separated by commas. In some of the examples there are redundancies but all of the notation is included for completeness. The usage parallels that suggested for κ.[4]



example 2, (2,2′-bipyridine-Ω*N*,*N*′)trimethyl(2,4-pentanedionato-Ω*C*³)platinum



example 3, dichloro[*N*,*N*-dimethyl-2,2′-thiobis(ethylamine)-Ω*S*,*N*′]platinum

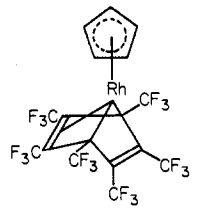


example 4, tris[2-(phenyldiazenyl-Ω*N*²)pyridine-Ω*N*]iron

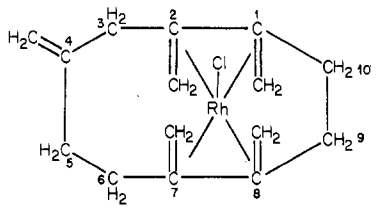
(c) Multidentate Ligands with Contiguous Ligand Atoms. These are denoted as above, citing the ligand atoms in sequence, each symbol being separated from its neighbor by a comma. Thus, bis(cyclopentadienyl)iron is bis(cyclopentadienyl-Ω*C*¹,*C*²,*C*³,*C*⁴,*C*⁵)iron. This is simplified where the donor atoms are all of the same kind and the numbering is inclusive: bis(cyclopentadienyl-Ω*C*¹–*C*⁵)iron. As a final simplification, where all the atoms of a chain or ring are of the same kind and are all involved in bonding to a metal, this can be further reduced to bis(cyclopentadienyl-Ω⁵)iron.[9] Note in example 6 (and example 8) that the *hapto* olefins are not explicitly cited because the individual ligating carbon atoms of the olefin come in different parts of the name.

(d) Multinuclear Complexes. It is possible to name multinuclear complexes unequivocally by an adaptation of the procedure already described. This is done by citing the nuclear atom symbol after the part of the ligand name which designates that part of the ligand to which it is attached, but before the Ω. An example, but a redundant use in a mononuclear complex, would be to name bis(cyclopentadienyl)iron as follows: bis(cyclopentadienyl-Fe Ω*C*¹–*C*⁵)iron.

In a dinuclear complex, the citing of nuclear atoms may become necessary to define the structure completely. Where ligands are bridging the name can be prefixed as classically, by μ. Alternatively, or additionally, the metal atoms may be cited twice, either before μ as a prefix or before Ω. In the last case, μ becomes redundant, but may well be retained as an

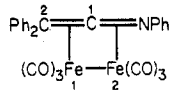


example 5, (cyclopentadienyl-Ω⁵)[hexakis(trifluoromethyl)-benzene-Ω*C*¹–*C*⁴]rhodium

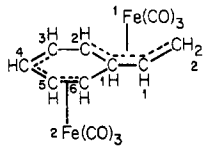


example 6, chloro[4-methylene-1,2,7,8-tetrakis(methylene-Ω*C*)cyclododecane-Ω*C*¹,*C*²,*C*⁷,*C*⁸]rhodium

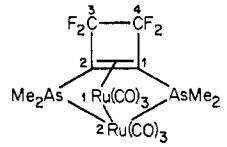
indicator. The procedure is that ligands are cited in alphabetical order (IUPAC rules,[2] 7.25). The metal atoms are assigned numerical designators in an arbitrary fashion, but the order is irrelevant when the metal atoms and their subsidiary ligands are identical.



example 7, 1,1,1,2,2,2-hexakis(carbonyl-Ω*C*)[*N*-(diphenylethenylidene-1Ω*C*¹,*C*²:2Ω*C*²)aniline-2Ω*N*]diiron(*Fe–Fe*)



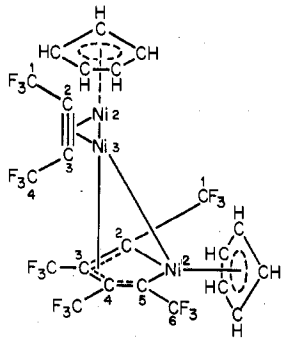
example 8, 1,1,1,2,2,2-hexakis(carbonyl-Ω*C*)[(ethenyl-1Ω*C*¹,*C*²:2Ω*C*³–*C*⁶]diiron



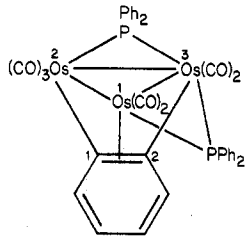
example 9, 1,1,1,2,2,2-hexakis(carbonyl-Ω*C*)[(3,3,4,4-tetrafluoro-1-cyclobutene-1,2-diyl-1Ω*C*¹,*C*²]bis(dimethylarsine-2Ω*As*)]-diruthenium(*Ru–Ru*)

Where the coordination shells (apart from the complex ligand attachments) are different, then the problem of order of citation of nuclear atoms is no longer trivial. It is suggested that the numerical order should be defined by the order in which the atoms appear in the name, this being determined in turn by the names of the ligands. However, there is no agreed general way of deciding the order. The naming device suggested does, however, produce unequivocal names even though they may not be unique. In example 10, the order of metal citation is determined unequivocally by the ligands. In example 11, variations in the osmium numbering are permitted on the present system. A simplification using atom designators and μ could relieve the double citation of diphenylphosphido—i.e., 1,3:2,3-bis[μ-diphenylphosphido-Ω*P*,Ω*P*]. This needs fuller investigation.

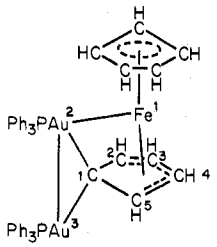
Where more than one kind of nuclear atom is encountered, Table IV of the IUPAC rules[2] can be used to determine priorities. This is shown in example 12, in which Fe is un-



example 10, 1,2-bis(cyclopentadienyl-Ω^5)[1,1,1,6,6,6-hexafluoro-3,4-bis(trifluoromethyl)-2,4-hexadiene-2,5-diyl-1ΩC^2,C^5:3ΩC^2-C^5](hexafluorobut-2-yne-2ΩC^2,C^3:3ΩC^2,C^3)trinickel(Ni^1-Ni^3,Ni^2-Ni^3)



example 11, [1,2-benzenediyl-1ΩC^1,C^2:2ΩC^1:3ΩC^2]-1,1,2,2,2,3,3-heptakis(carbonyl-ΩC)(diphenylphosphido-1,3ΩP)(diphenylphosphido-2,3ΩP)-*triangulo*-triosmium(3*Os*-*Os*)



example 12, (1,1-cyclopentadienediyl-1ΩC^2-C^5:2ΩC^1:2,-3ΩC^1)-1-(cyclopentadienyl-Ω^5)-2,3-bis(triphenylphosphine)-1-iron-2,3-digold(1+)(*Fe*-*Au*,*Au*-*Au*)

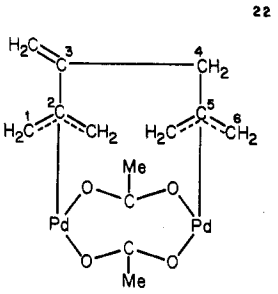
equivocally given the locator 1.

Examples 13, 14, and 15 show further names derived on the basis of the above ideas. Example 15 could be simplified by using μ. For instance, devices such as "1,3:1,3:2,4:2,4-tetra-μ-chloro" would avoid the repetition of the chloro citation. Since chloro ligands are monatomic, 2,4ΩCl seems unnecessary.

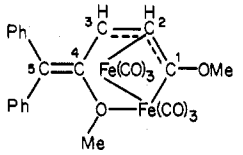
Conclusions

The "κ plus η" convention of Busch and Sloan[4] is a considerable advance in the methods of designating structures of compounds containing complex ligands. There appears to be little advantage, however, in retaining both designators with different formatting procedures when one will do. Hence it is suggested that a single new convention be adopted. The use of η has the advantage that it does signal the presence of contiguous ligating atoms even where the name does not, but the value of this is disputable, and the chemical significance is rarely clear and has nothing to do with nomenclature. In any case, η has already been corrupted in usage. The Ω convention avoids these kinds of problems.

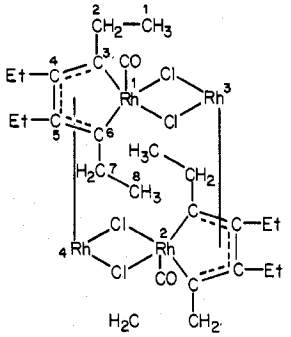
The numbering system used to name some of the complicated ligand skeletons used in the examples is not necessarily that which may be adopted finally by IUPAC. The principle of the Ω convention is not dependent on the numbering systems finally agreed upon, for either the ligand skeletons or the polynuclear metal clusters.



example 13, bis(acetato-1ΩO:2$\Omega O'$)[3-methylene-2-(methylene-1ΩC)-5-(methylene-2ΩC)-1,6-hexanediyl-1ΩC^1,C^2:2ΩC^5,C^6]-dipalladium



example 14, 1,1,1,2,2,2-hexakis(carbonyl-ΩC)[1-methoxy-4-(methoxy-1ΩO)-5,5-diphenyl-2,4-pentadiene-1,3-diyl-1ΩC^1:2ΩC^1-C^3]diiron(*Fe*-*Fe*)



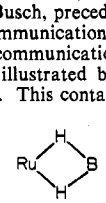
example 15, 1,2-bis(carbonyl-ΩC)bis(chloro-1,3Ω)bis(chloro-2,4Ω)(4,5-diethyl-3,5-octadiene-3,6-diyl-1ΩC^3,C^6:4ΩC^3-C^6)-(4,5-diethyl-3,5-octadiene-3,6-diyl-2ΩC^3,C^6:3ΩC^3-C^6)-tetrarhodium

The Ω convention with nuclear atom designators allows the possibility of naming polynuclear compounds by a straightforward and simple technique. It may be necessary to use an ad hoc system for numbering nuclear atoms until a rigorous system is developed, but in the meantime unequivocal though not unique names can be developed. The Ω convention could even be used to name cluster compounds. The names would be clumsy and such a possibility should not preempt efforts to find a more appropriate, systematic method.

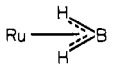
Acknowledgment. This paper was developed under the auspices of the Commission for the Nomenclature of Inorganic Chemistry of IUPAC and is published with its permission. It is a working document of CNIC published for comment and constructive criticism and is not IUPAC approved.

References and Notes

(1) "I.U.P.A.C., Nomenclature of Inorganic Chemistry (1957)", 1st ed, Butterworths, London, 1959.
(2) "I.U.P.A.C., Nomenclature of Inorganic Chemistry (1970)", 2nd ed, Butterworths, London, 1971.
(3) F. A. Cotton, *J. Am. Chem. Soc.*, **90**, 6230 (1968).
(4) T. E. Sloan and D. H. Busch, preceding paper in this issue.
(5) N. Lozac'h, personal communication.
(6) C. Gustafson, personal communication.
(7) The problems are well illustrated by the compound formulated as $[RuH(BH_4)(PMePh_2)_3]$. This contains the grouping



and the BH_4 group may be described as η^2 (Cotton), κ^2 (Sloan and Busch), or a bidentate ligand designated "tetrahydridoborate-*H,H'*" (IUPAC). Should one choose to write the grouping



it becomes η^3 (Cotton), η^3 (Sloan and Busch), or η (IUPAC).

(8) It has been customary to use small Greek letters to denote designators. I have used capital omega because it is unlikely to be confusing and the available small Greek letters are unsatisfactory. Should a small letter be insisted upon, I propose theta (θ).

(9) This does not prevent the informal description of a ligand as Ω^3, Ω^5, etc., as appropriate, however many atoms may compose the ligand part, but unless the usage for nomenclature purposes is severely restricted, considerable difficulties can arise.

Contribution from the Department of Chemistry, University of New Mexico, Albuquerque, New Mexico 87131

Enumeration of Isomers for Complexes Containing Multiple Elements of Stereoisomerism

ROBERT E. TAPSCOTT* and DRAGOSLAV MARCOVICH

Received December 20, 1977

The application of Pólya's counting theorem to determine the number of isomers possible owing to variations in absolute configuration of sites of stereoisomerism is presented. The method described, which is applicable even when different types of stereoisomerism are present, partitions the isomers into classes according to the distributions of absolute configurations among the stereoisomeric sites for a more complete enumeration and permits a determination of whether pseudoasymmetry is possible. Counting functions which allow a facile count of the total isomers possible and a computation of the number of meso structures when only chiral sites have a variable configuration are also presented. The method is illustrated by application to three series of compounds containing multiple sites of dissymmetry—octahedral chelates of bidentate ligands, dihydroxydicarboxylate-bridged binuclear complexes, and trans-octahedral and square-planar complexes of macrocycles.

Introduction

A number of papers have discussed the application of combinatorial methods to the enumeration of permutational isomers by means of Pólya's counting theorem[1-5] or the alternative formulation of Lunn and Senior.[6,7] It has not been recognized, however, that a treatment similar to that used to count permutational isomers can be applied to isomer counting for compounds containing multiple sites of stereoisomerism. In this application, rather than permuting ligands on a molecular skeleton, one permutes absolute configuration designations. In this way, isomerism arising from stereoisomeric elements within the molecular framework itself can be examined.

In this paper, we develop this method and apply it to an enumeration of isomers for three series of complexes containing multiple chiral sites which have been counted in the literature by other, more laborious techniques. Although the present technique is illustrated only for metal ion complexes with dissymmetric sites, it can be used for other systems with other types of stereoisomerism under the restrictions discussed herein.

Procedure

The isomers which may be enumerated by the methods developed here are those which arise owing only to variations in absolute configuration in one or more molecular elements of stereoisomerism.[8] Isomers resulting from other factors such as ligand permutations and skeletal rearrangements must be enumerated separately. We employ the terms "elements of stereoisomerism" and "stereoisomeric sites" interchangeably since the only elements which can be treated by the method described are those which occupy a definite molecular site (though not necessarily a stereoisomeric center[8]). In general, the terms "site" and "element" are restricted to those elements whose absolute configurations are allowed to vary for the isomer enumeration. Invariant elements are included in the skeleton (vide infra). All variable stereoisomeric elements taken into account in one specific step of an isomer enumeration must have the same number (k) of possible configurations. In most cases, and in all examples given here, $k = 2$. The elements must be such that their absolute configurations could be unambiguously specified using either accepted descriptors such as "*R,S*"[9] or "*E,Z*"[10] or any arbitrary but unambiguous designations. An absolute configuration designation for one stereoisomeric site must in no way depend upon the designations of configuration at other sites.

We define the molecular skeleton as the entire molecule whose isomers are to be enumerated with the symmetry it would have if all of the variable-configuration elements were of such a geometry that stereoisomerism were impossible. In the case of chiral elements this is best realized by treating each such element as though it were planar. Skeletons defined in this way are related to the more restrictive two-dimensional projection formulas employed by others to enumerate isomers in some selected bridged chelates.[11] That the skeletal symmetry may change once absolute configurations are assigned (e.g., planar, achiral elements become nonplanar and chiral) is of no more or no less significance than the fact that the symmetry of a molecule for which permutation isomers are counted by standard combinatorial methods[1-5] may change with a permutation of the ligands. Only the initial skeletal symmetry needs to be considered.

Once a skeleton has been chosen, it must remain invariant. Each change involving the absolute configuration of an element of stereoisomerism which has not been included among the variable-configuration elements or involving any change in connectivity of atoms requires that another count be made with the new basic skeleton.

A key point in the enumeration of isomers owing to the presence of elements of stereoisomerism of more than one kind is the following. A descriptive label for absolute configuration can be considered to have meaning only when it is associated with a particular site. Thus, we can label sites as "possibility 1", "possibility 2", ..., "possibility k" and relate these labels, if desired, to more familiar designations once the site associated with each label is considered. This permits us to permute all designations among all sites of stereoisomerism rather than restricting, e.g., *E,Z* descriptors to cis–trans sites. Without this convention, the method presented would be much less useful. We will employ the configuration designations α and β in the examples presented. An extension to (rare) molecular

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