

to be located on the chlorine atoms in the ground-state $2a_2$, $11e$ (t_1) and $14a_1$, $9e$ ($6t_2$) molecular orbitals. Therefore, the appearance of the ν_3 satellite mode is expected. However, the presence of the ν_1 mode indicates a strong oxide character in either the $9e \rightarrow 12e$ component of the $5t_2 \rightarrow 2e$ excitation (T_d parentage) or the $2a_2$, $11e \rightarrow 13e$ components of the $1t_1 \rightarrow 7t_2$ excitation (T_d parentage). This is unexpected considering the charge density distribution in the orbitals comprising these excitations (cf. Table VI). However, such behavior is observed for the $5t_2 \rightarrow 2e$ excitations in MnO_3Cl and MnO_2Cl_2 . The $L \rightarrow M$ charge transfer assigned to this region is therefore a $p\pi \rightarrow d\pi^*$ (chlorine \rightarrow manganese) interaction with some $p\pi \rightarrow d\pi^*$ (chlorine \rightarrow oxygen or chlorine \rightarrow manganese) charge transfer also likely.

Acknowledgment. The authors wish to acknowledge the support of the National Science Foundation (Grants GP-15432A1 and GP-41506) and the Research Corp. Dr. John H. Wood is thanked for providing the SCF- $X\alpha$ -SW computer program used in our molecular orbital calculations.

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Stereochemical Notation in Coordination Chemistry. Mononuclear Complexes

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A unified system of notation for geometric isomers, including central atom symmetry and optical isomers for mononuclear complexes, is presented for known geometries up to coordination number 6. This notation system makes extensive use of the complementary features of the Cahn, Ingold, and Prelog (CIP) system for tetrahedra, the IUPAC helical system for bis- and tris-chelated octahedra, and a proposal by Petrarca, Rush, and Brown using CIP priority ranking to describe stereoelements in a unified and general manner. This system has been introduced in the Indexes to *Chemical Abstracts* starting with Volume 76 (January–June 1972). Certain aspects of ligand stereochemistry and the notation for ferrocene complexes are discussed.

Introduction

The concept of the geometric arrangement of groups around a central atom or ion has been a central precept of coordination theory since its early development by Alfred Werner starting in 1893. The ideas of coordination number and the specific geometric arrangement of ligands (symmetry) are among the first encountered by the student of coordination chemistry. In a verbal discussion between coordination chemists, the terms "square planar", "octahedral", and "tetrahedral" are as often heard as "isomer", "molecule", or "ion". Formal nomenclature, however, has skirted the development of names or notations which give explicit designations to the symmetry of a complex. Thus, when the coordination chemist writes *cis*-diamminedichloroplatinum, previous chemical experience and logic imply that the compound has a square-planar configuration. The indirect implication of the configuration of a complex has not greatly hindered formal communication in coordination chemistry up to now because one type of symmetry predominated, except for coordination numbers 4 and 5. In these latter two instances experience in the area led to generalizations of the accepted symmetries in a specific system and the exceptions to the generalizations became well known. However, with the growth of coordination chemistry in the last three decades, the number of symmetries and notations proposed and used in formal communication has increased to match the growth in the field.

In the recent literature, various stereochemical notations

for coordination compounds have been suggested.²⁻¹¹ The most general systematic approach to stereochemical notation is the Cahn-Ingold-Prelog (CIP) standard sequence rule⁷ which has been used with great success for the several classes of chirality encountered in organic chemistry.

The standard sequence rule is the procedure in which the ligands are ranked in order of precedence, hereafter referred to as seniority, on the three-dimensional model of the molecule. The chiral element is given a symbol representing the handedness of the progression of the seniorities of the ligands. For the case of the nearly tetrahedral carbon center encountered frequently in organic chemistry, the molecule is viewed from the side opposite the least-senior (largest priority number) ligand and the symbols *R* (right-handed or clockwise) and *S* (left-handed or anticlockwise) are used to indicate the direction of the progression of the seniorities.

The seniorities are determined according to the subrules given in ref 7: (1) higher atomic number precedes lower; (2) higher atomic mass number precedes lower; (3) *Z* precedes *E*;¹² (4) like pair *R,R* or *S,S* precedes unlike *R,S* or *S,R*; ...; (5) *R* precedes *S*....

In the application of these subrules the ligands are arranged in order of decreasing atomic number. For the case of a tetracoordinate center with the ligands H, Cl, Br, and F, the ligands are ranked $35 > 17 > 9 > 1$, $Br > Cl > F > H$, and the relative priority numbers $Br = 1$, $Cl = 2$, $F = 3$, and $H = 4$ are used to determine the clockwise or anticlockwise sense

Table I. Exploration Table (by Atomic Number)

	Steps		
	1	2	3
①			
②			
③			
④			
⑤			
⑥			
⑦			

of direction for the progression for a tetrahedral four-coordinate system.

Complexes with polyatomic ligands frequently require differentiation of identical donor atoms. When several ligands have the same donor atom, it is necessary to consider their substituents. The following examples demonstrate our use of the CIP standard sequence rule subrule 1 in assigning priority numbers. The priority numbers are shown in the figures. It should be noted that the higher the seniority, the smaller the priority number. The ligand structures in the exploration tables (Tables I and II) have been redrawn with atomic numbers rather than the element symbols representing the atoms.

According to CIP standard sequence rule, all atoms other than hydrogen are complemented to quadriligancy or higher ligancy by providing them, if necessary, with imaginary bonds and atoms. In those cases where one atom has two or more doubly bound attachments, higher ligancies are shown (see the nitrate ligand in Table II). They are provided with one or two "duplicate" representations of any atoms to which they are doubly or triply bonded, respectively; and their unsaturation, if any, of unshared valence electrons is satisfied with "phantom" atoms of atomic number zero. In comparing the substituents around an asymmetric tetrahedral atom or a central atom of a complex, one always proceeds outward. Each bonding or donor atom is attached to the same center and taking this central atom into consideration would never provide any distinction between the attached atoms. Similarly, the electron pair with which the donor atom forms a bond to a central atom is also not counted. However, if a donor has any unshared electron pairs, these are considered to be phantom

Table II. Exploration Table (by Atomic Number)

	Steps			
	1	2	3	4
①				
②				
③				
④				
⑤				
⑥				
⑦				
⑧				
⑨				
			Average	
			$6 \frac{1}{2} (3.5)$	

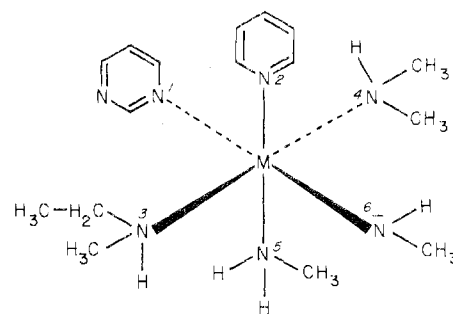


Figure 1. Illustration of assignment of CIP relative priority numbers for ligands.

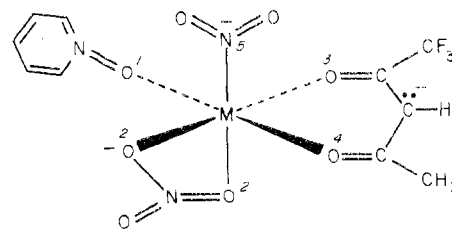


Figure 2. Illustration of assignment of CIP relative priority numbers for ligands.

atoms of atomic number zero (see the methylamino ligand in Table I). Thus, ignoring the bond to the central atom, the donor atoms themselves are complemented only to triligancy, although in a few cases, as the nitro group in Table II, the ligancy could be higher. In the case of aromatic heterocyclic

ligands with resonating double bonds, each duplicate representation is given an atomic number that is the mean of the two it would have had if the double bond were located at each of the possible positions.

The atoms attached to a donor atom are arranged in order of decreasing seniority in the exploration tables (Tables I and II). Atomic numbers in parentheses are the duplicate representations for the doubly bonded carbons, nitrogens, and oxygens.

In comparing the five oxygen donors in Table II note that only those electron pairs that are not used in bonding to the central atom are counted as phantom atoms. In chelating carboxy and inorganic oxo anions, such as nitrate, the oxygen atoms are treated as equivalent because of resonance. Therefore, after exploring the attachments to each of the bonded nitrate oxygens, we combine the two sets and take the average. This average set is then compared with the set of atoms attached to the oxygen on pyridine 1-oxide; the latter, being more senior, is given priority number 1 and the nitrate oxygens are given priority number 2. The two ketone oxygens were shown to be less preferred than the pyridine 1-oxide and nitrate oxygens in step 2 but their exploration must be continued in order to choose the more preferred. It should be noted that in β -diketonate ligands the delocalized negative charge is assigned to the carbon between the two carbonyl groups, giving a symmetrical representation. In the third exploration step the most preferred atom in both cases is a duplicate oxygen (shown in the curves in the exploration tables), and since duplicate atoms have no substituents, the second preferred atoms of each group must be compared in step 4. This step provides a distinction between the two ketone oxygens. They are assigned priority numbers 3 and 4. The nitrogen donor is given priority number 5.

It is not necessary to draw out the exploration tables in most cases since it is usually possible to distinguish identical donors by inspection.

This paper will demonstrate that the CIP method for tetrahedral centers can also be used to rank donor atoms in coordination compounds. This method of assigning priority numbers to donor atoms plus a subrule to distinguish identical priority numbers and a symmetry site term form the basis of the notation system. This notation system has been introduced for mononuclear coordination compounds in Volume 76 (1972) *Indexes to Chemical Abstracts* for the Ninth Collective Period (1972-1976).

Illustration of Principles

The stereochemical descriptors given in this system are comprised of four parts: (a) a symmetry site term, (b) a configuration number, (c) a chirality symbol, and (d) a ligand segment.

The symmetry site term is a one or two letter code to express the idealized molecular geometry about the central atom. The symmetry site terms are derived directly from commonly used geometric descriptive terms (tetrahedral, square planar, trigonal bipyramidal, square pyramidal, octahedral, and trigonal prismatic) and the coordination number of the metal: *T*-4, *SP*-4, *TB*-5, *SP*-5, *OC*-6, *TP*-6. (Note that *SP*-4 is square planar, four-coordinate; *SP*-5 is square pyramidal, five-coordinate.) The symmetry site terms are assigned as closely as possible to the overall idealized geometry of the coordination center. Distortions from idealized geometry occur widely in nature for many reasons, crystal-packing considerations, varying sizes of ligands, etc. However, as has been noted recently,¹³ coordination compounds tend toward one or another of two or more idealized models for a given coordination number. Quantitative parameters such as the θ parameter noted in ref 13 will undoubtedly prove useful to crystallographers and others who have available precise atomic and

molecular coordinate data. However the description of the geometry of most molecules reported in the present literature is based on qualitative data. Thus, the widely accepted practice of relating molecular structures to idealized models seems to be the most practical and widely recognized principle on which to base a *qualitative* notation.

The configuration number is a one- to three-number expression used to identify atoms on symmetry elements of a structure and in this way distinguish geometric isomers. Configuration numbers are derived from priority numbers assigned by application of the CIP standard sequence rule. The degeneracy resulting from the identity of coordinating atoms or groups (giving identical CIP priority numbers) is resolved by observing the following principles.

(1) **The Trans Maximum Difference Subrule.** The same relative priority numbers are assigned to all constitutionally equivalent atoms. For example, in the system $Ma_2b_2c_2$ (where *M* is a central atom and *a*, *b*, and *c* represent monodentate ligands), the relative priority numbers are 1, 1, 2, 2, 3, 3. Whenever a choice exists in distinguishing between constitutionally equivalent donor atoms, the preference is given to the donor atom trans to the donor of highest CIP priority number. In this way configuration numbers can be chosen based on the symmetry characteristics of a particular geometry to distinguish between the position isomers of any geometry through coordination six by giving a number no more than three digits in length.

(2) **Priming Subrule a.** When there are two or more equivalent bidentate or tridentate ligands, e.g., $M(AA)_3$, $M(AB)_3$, and $M(BAB)_2$ (where *M* is a central atom and *AA*, *AB*, and *BAB* represent polydentate chelating ligands) and the same priority numbers thus occur in equivalent ligands, the ties are broken by identically priming, double priming, etc. all the CIP priority numbers of ligating atoms within a ligand to determine both the configuration number and the chirality symbol.

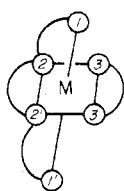
Priming Subrule b. In the cases of symmetrical tetradentate, pentadentate, and hexadentate ligands, ties between equivalent ligating atoms are broken, where necessary, by priming ligating atom priority numbers in half of the ligand. When two or more nonequivalent tie-breaking choices exist, the tie is broken by application of the trans maximum difference subrule. Primed ligating atom priority numbers are less preferred (higher value) than those which are unprimed but are of the same absolute value; doubly primed priority numbers are less preferred than primed, etc. The primes are not included in the configuration number except when absolutely necessary, e.g., for octahedral complexes containing two identical tridentate ligands and trigonal-prismatic complexes containing two or more identical polydentate ligands.

The chirality symbols *C* (clockwise) and *A* (anticlockwise) are used to denote absolute stereochemistry in coordination compounds, except that *R* and *S* are used for tetrahedral complexes (*T*-4) and Δ and Λ for octahedral complexes with three bidentate or two bidentate ligands in a skew configuration.¹⁴

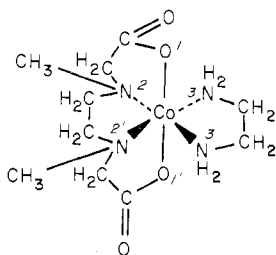
Ligand stereonotation, except for stereoparents,¹⁵ is set off in enclosing marks and given after the central metal atom stereonotation (see Figures 5 and 6). When it is necessary to associate a locant with the ligand stereonotation to avoid ambiguity, the CIP priority number of the ligating atom is used as the locant. The lowest CIP priority number is used for polydentate ligands. Stereodescriptors for stereoparents are cited in the ligand portion of the name, as in Figure 6.

Assignment of Configuration Numbers and Chirality Symbols

A. Six-Coordination. 1. Octahedral (OC-6). For the octahedral structure the symmetry code *OC* and the coor-

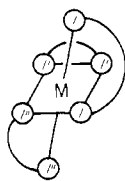


configuration number = 13
chirality symbol = *A*

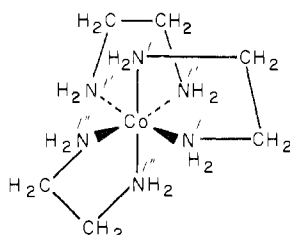


(*OC-6-13-A*)-[1,2-ethanediamine-*N,N'*][[*N,N'*-1,2-ethanediamylbis-(*N*-methylglycinato)](2-)-*N,N'*,-*O,O'*]cobalt(1+)

Figure 3. $[\text{Co}(\text{en})(\text{C}_8\text{H}_{14}\text{N}_2\text{O}_4)]^{3+}$.



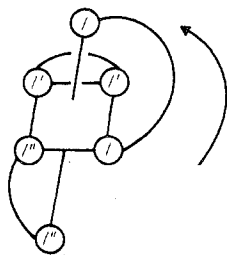
configuration number = 11
chirality symbol = Δ



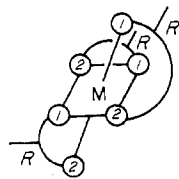
(*OC-6-11-Δ*)-tris(1,2-ethanediamine-*N,N'*)cobalt(3+)

Figure 4. $[\text{Co}(\text{en})_3]^{3+}$.

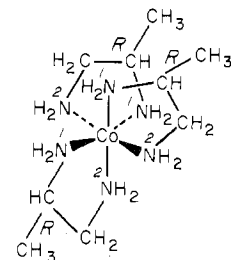
dination number 6 are assigned. The first digit of the two-digit configuration number is the CIP priority number of the ligating atom trans to the most preferred ligating atom of priority number 1. These two atoms define the principal axis of the octahedron. The second digit of the configuration number is the CIP priority number for the ligating atom trans to the most preferred ligating atom of lowest CIP priority number in the plane perpendicular to the principal axis (see Figures 3–6). The chirality symbol *C* is assigned to that configuration in which the CIP priority numbers of the ligating atoms in the plane increase proceeding in a clockwise direction when viewing the plane from the most preferred atom of CIP priority 1 on the principal axis. The opposite configuration is assigned the chirality symbol *A* (see Figure 3). Octahedral complexes with three bidentate ligands or two bidentate ligands bonded in a skew configuration are an exception. In these latter cases the configuration numbers are assigned as described, but the chirality symbols Δ and Λ are assigned according to the IUPAC rule 7.8¹⁴ (see Figures 4–6). The chirality symbols *C* and *A* could also be used by observing the priming principles given in priming subrule a. According to this subrule, the structure in Figure 4 would be as illustrated and would be given



the notation (*OC-6-11-A*)-tris(1,2-ethanediamine-*N,N'*)cobalt(3+). The total stereochemistry is cited by placing the descriptors in order, separated by hyphens and enclosed in parentheses. The utility of CIP standard sequence rule combined with the three subrules given here can best be illustrated in the general case of a $[\text{Ma}_2\text{bcde}]$ octahedral structure which has nine geometric isomers, with CIP relative



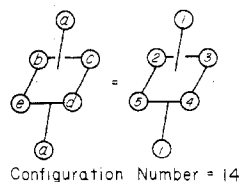
configuration number = 21
chirality symbol = Δ



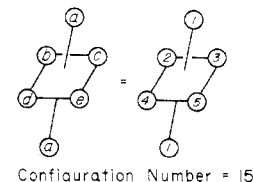
(*OC-6-21-Δ-(R),(R),(R)*)-tris(1,2-propanediamine-*N,N'*)cobalt(3+)

Figure 5. $[\text{Co}(1,2\text{-pn})_3]^{3+}$.

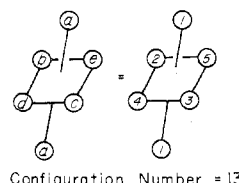
Table III. $[\text{Ma}_2\text{bcde}]$ Octahedral Isomers



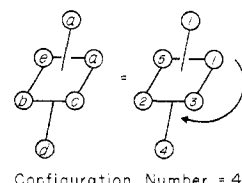
Configuration Number = 14



Configuration Number = 15

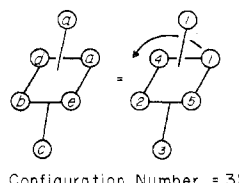


Configuration Number = 13



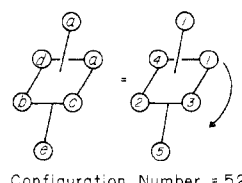
Configuration Number = 42

Chirality Symbol = *C*



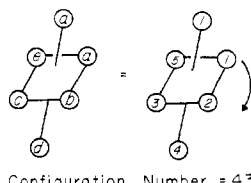
Configuration Number = 32

Chirality Symbol = *A*



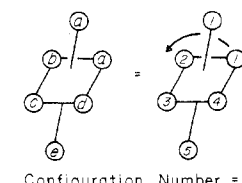
Configuration Number = 52

Chirality Symbol = *C*



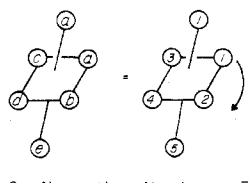
Configuration Number = 43

Chirality Symbol = *C*



Configuration Number = 53

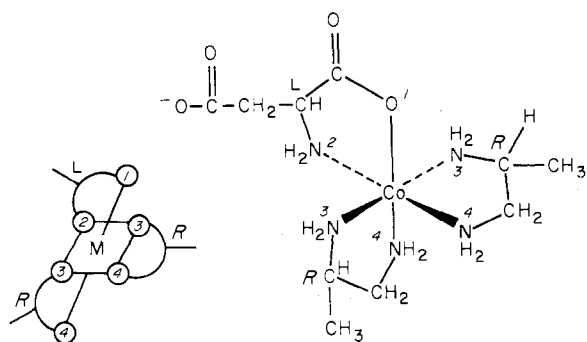
Chirality Symbol = *A*



Configuration Number = 54

Chirality Symbol = *C*

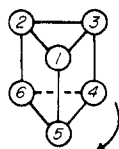
* (Note preference is given to the axis with the highest CIP priority number opposite 1)



configuration number = 44
chirality symbol = Λ

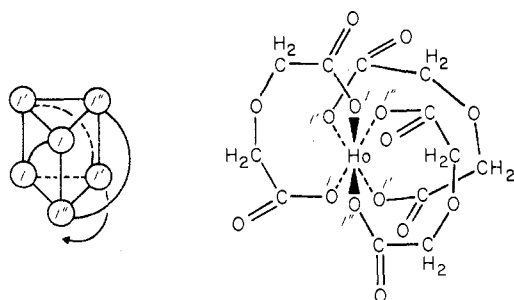
[OC-6-44- Λ -(*R*),(*R*)]-[L-aspartato-(2-)-*N*,*O*¹]bis(1,2-propanediamine-*N,N'*)cobalt(1+)

Figure 6. [Co(C₄H₅NO₄)(1,2-pn)₂]⁺.



configuration number = 564
chirality symbol = *C*

Figure 7.



configuration number = 1''11'
chirality symbol = *C*

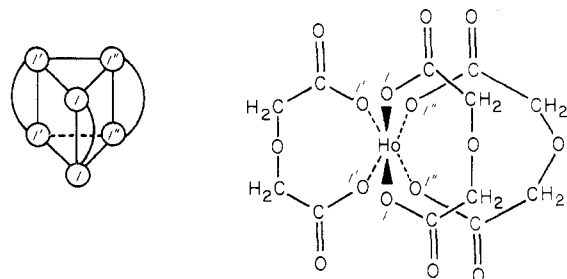
(*TP*-6-1''11'-*C*)-tris[[2,2'-oxybis(acetato)](2-)-*O*¹,*O*^{1'}]holmate(3-)

Figure 8. [Ho(C₄H₄O₅)₃]³⁻.

priority numbers of a = 1, b = 2, c = 3, d = 4, and e = 5 (see Table III).

2. Trigonal Prismatic (*TP*-6). For the trigonal-prismatic structure the symmetry code *TP* and the coordination number 6 are assigned. The configuration number is derived from the CIP priority numbers opposite the triangular face containing the greater number of ligating atoms of smallest CIP priority number. When both triangular faces contain the same number of ligating atoms of lowest CIP priority number, the preferred triangle is the one containing the greater number of ligating atoms of second lowest priority numbers. This process is continued until the tie is broken or the triangular faces are deemed equivalent. The configuration number is given by citing the CIP priority numbers of the atoms eclipsed by the preferred triangular face in the same order, from lowest to highest priority number, as they occur in the preferred triangular face (see Figures 7-9). The chirality symbols *C* and *A* are assigned by viewing the trigonal prism from above the preferred triangular face and noting the direction of progression of the priority numbers for the less preferred triangular face (see Figures 7 and 8). The configuration number 1''11' is preferred to 1'1'1 in Figure 8 because this places the ligating atom of lowest CIP priority number opposite the ligating atom of highest priority number (the doubly primed one). See the trans maximum difference subrule.

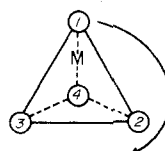
B. Four-Coordination. 1. Tetrahedral Geometry (*T*-4). For



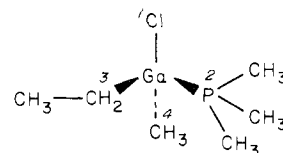
configuration number = 11'1''

(*TP*-6-11'1'')-tris[[2,2'-oxybis(acetato)](2-)-*O*¹,*O*^{1'}]holmate(3-)

Figure 9. [Ho(C₄H₄O₅)₃]³⁻.

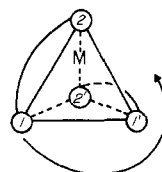


chirality symbol = *R*

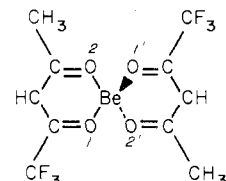


(*T*-4-*R*)-chloroethylmethyl(trimethylphosphine)gallium

Figure 10. [GaCl(C₂H₅)(CH₃)[(CH₃)₃P]].

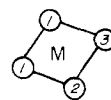


chirality symbol = *S*

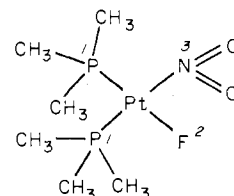


(*T*-4-*S*)-bis(1,1,1-trifluoro-2,4-pentanedionato-*O,O'*)beryllium

Figure 11. [Be(C₅H₄F₃O₂)₂].



configuration number = 3



(*SP*-4-3)-fluoro(nitrito-*N*)-bis(trimethylphosphine)platinum

Figure 12. [PtF(NO₂)[(CH₃)₃P]₂].

tetrahedral geometry the symmetry code *T* and the coordination number 4 are assigned. No configuration number is required for tetrahedral compounds. The chirality symbols *R* and *S* are assigned by the CIP standard sequence rule (see Figure 10). The *R*, *S* notation for tetrahedral chelated complexes is derived according to the rules presented in ref 7, Section 2.5, which represents the tetrahedral application of priming subrule a (see Figure 11).

2. Square Planar (*SP*-4). For square-planar geometry the symmetry code *SP* and the coordination number 4 are assigned. The configuration number is the CIP priority number for the ligating atom trans to the most preferred atom of CIP priority number 1 (see Figure 12).

C. Five-Coordination. 1. Trigonal Bipyramidal (*TB*-5). For the trigonal-bipyramidal structure the symmetry code *TB* and the coordination number 5 are assigned. The two-digit configuration number consists of the CIP priority numbers for the two ligating atoms on the major axis (axial positions), the atom of lowest CIP priority number being given first. For compounds of this structure with no reflection symmetry, the chirality symbols *C* and *A* are given by viewing the plane from

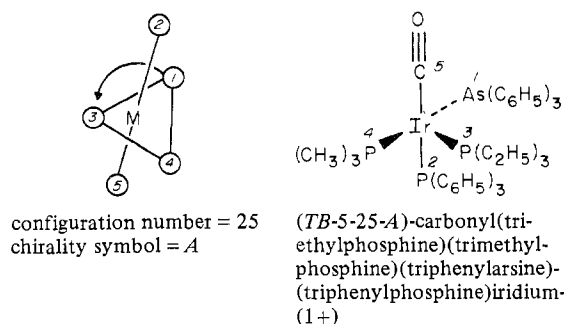
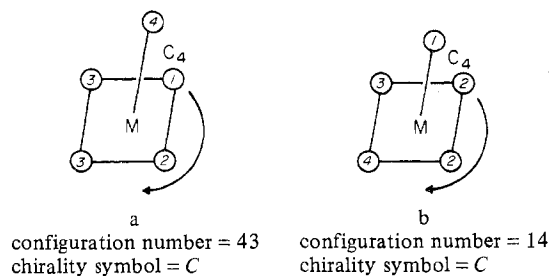
Figure 13. $[\text{Ir}(\text{CO})[(\text{C}_2\text{H}_5)_3\text{P}][(\text{CH}_3)_3\text{P}][(\text{C}_6\text{H}_5)_3\text{As}][(\text{C}_6\text{H}_5)_3\text{P}]]^+$.

Figure 14.

the ligating atom of smallest CIP priority number on the principal axis as described for the octahedral geometry (see Figure 13).

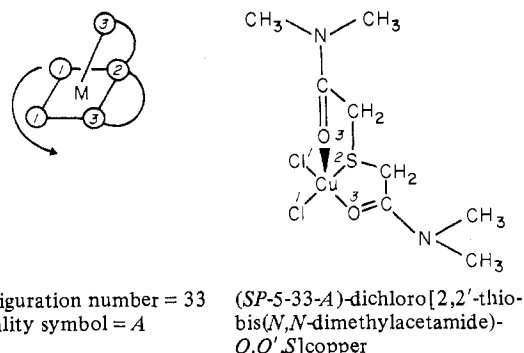
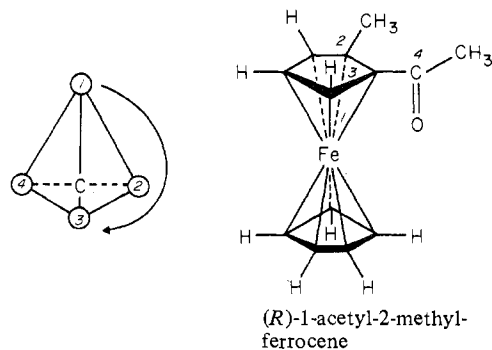
2. Square Pyramidal (*SP-5*). For the square pyramid the symmetry code *SP* and the coordination number 5 are assigned. The two-digit configuration number consists of the CIP priority number for the ligating atom on the principal axis, followed by the CIP priority number for the coordinating atom opposite the most preferred ligating atom of lowest CIP priority number in the plane. The chirality symbol *C* is assigned to that configuration in which the CIP priority numbers of the ligating atoms in the plane increase proceeding in a clockwise manner when viewing the plane from the ligating atom on the C_4 axis. (See Figure 14a.) The opposite configuration is assigned the chirality symbol *A*. For structures which contain the two lowest priority number ligating atoms in the plane (see Figures 14b and 15), the most preferred is determined by the trans maximum difference subrule.

D. Metallocenes [bis(η^5 -2,4-cyclopentadien-1-yl)metal Complexes]. The extended Cahn-Ingold-Prelog system is now widely used in assigning chirality symbols to asymmetrically disubstituted metallocenes.¹⁶ *Chemical Abstracts* uses the sequence rule, which assigns the chirality symbols *R* and *S* to the chiral center of lowest CIP priority number in asymmetrically polysubstituted metallocenes whose absolute configurations are reported. (The configuration of the other four centers is then fixed.) (See Figure 16.)

Conclusion

The stereochemical notation being used in the Ninth Collective Indexes (1972-1976) to *Chemical Abstracts* for mononuclear complexes of coordination numbers 4-6 and representing six geometries and metallocenes has been presented with illustrative examples. This notation augments the general principles of chemical nomenclature and is compatible with other stereochemical notation used by *Chemical Abstracts* Service in its computerized processing of chemical information.

The evaluation of present and future proposals for the

Figure 15. $[\text{CuCl}_2(\text{C}_8\text{H}_{16}\text{N}_2\text{O}_2\text{S})]$.Figure 16. $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{C}_8\text{H}_9\text{O})]$.

extension of stereochemical notations to higher coordination numbers, π complexes (other than metallocenes, which are given above), and polynuclear complexes¹⁷ will continue. The goal of this continued effort will be to incorporate specific notations for these complexes into the information system of *Chemical Abstracts* Service and the indexes to *Chemical Abstracts*.

References and Notes

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