

Stereoisograms of Octahedral Complexes. I. Chirality and *RS*-Stereogenicity

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Abstract

The stereoisogram approach, which has originally been developed to rationalize organic stereochemistry (S. Fujita, *J. Org. Chem.*, **69**, 3158–3165 (2004); S. Fujita, *Tetrahedron*, **62**, 691–705 (2006); **65**, 1581–1592 (2009)), is extended and applied to inorganic stereochemistry by using octahedral complexes as examples. Stereoisograms of octahedral complexes are constructed and discussed in terms of attributive terms (chirality/achirality, *RS*-stereogenicity/*RS*-astereogenicity, and sclerality/asclerality) or equivalently in terms of relational terms (enantiomeric/self-enantiomeric, *RS*-diastereomeric/self-*RS*-diastereomeric, and holantimeric/self-holantimeric). After they are categorized into five types (Types I–V), stereoisograms of Type I, III, and V are shown to be characterized by *A/C*-descriptors, where the capability of giving *A/C*-descriptors is ascribed to *RS*-stereogenicity (or *RS*-diastereomeric relationships), which is determined to be a common nature to Types I, III, and V. Several textbook errors are pointed out and corrected in terms of the stereoisogram approach. For example, although the symbols *A* and *C* are originally called “chirality symbols” in the IUPAC recommendations 2005 (so-called The Red Book), the naming is inadequate and they should be called “*RS*-stereogenicity symbols”.

1 Introduction

Since the proposal of the coordination theory by Werner [1, 2], the stereochemistry of octahedral complexes has been one of central interests in inorganic stereochemistry, as found in a review [3]

and textbooks [4, 5]. Among various targets of inorganic stereochemistry, in general, problems concerned with enumerational and symmetrical properties have attracted continuous attentions of inorganic and theoretical chemists. This holds true for the stereochemistry of octahedral complexes as a branch of inorganic stereochemistry.

As for enumerational problems, Pólya's theorem [6, 7] and computer enumeration [8, 9] have been applied to count octahedral derivatives in parallel ways to organic stereochemistry. The methodology for such enumerational problems has been renewed by introducing the unit-subduced-cycle-index (USCI) approach [10], where the original formulation of the USCI approach for organic compounds has been successfully applied to the enumeration of octahedral complexes [11, 12].

On the other hand, symmetry problems of octahedral complexes have been restricted to rather straightforward applications of the conventional methodology of organic stereochemistry. For example, the section title "Describing absolute configuration — distinguishing between enantiomers" of the IR-9.3.4 of the IUPAC recommendations 2005 [13] implies that the *C/A*-system for describing absolute configurations of octahedral centers aims at referring to "chirality". This is parallel to the state of the art for the *R/S*-stereodescriptors of the Cahn-Ingold-Prelog (CIP) system for organic compounds, where the usage of the term "chirality center" is maintained though the term "stereogenic" was adopted as its theoretical basis in place of "chiral" [14]. Moreover, the concept of "prochirality" for treating organic compounds [15, 16] has been applied to the discussion on prochirality of coordination compounds [17]. Thus the original formulation for organic compounds has been unconsciously postulated to be a geometrical concept (cf. the term "prochirality" of the IUPAC Basic Terminology of Stereochemistry [18]) and has been applied to coordination compounds. In other words, confused situations between "chirality" and "stereogenicity" as well as between "prochirality" and "prostereogenicity" (or "prostereoisomerism") in organic stereochemistry (cf. [19]) have been unconsciously brought into inorganic stereochemistry.

The confused situations in organic stereochemistry have been avoided by *stereoisograms*, which was proposed by us to comprehend stereochemical phenomena [20–22]. Thus, a quadruplet of *RS*-stereoisomeric (pro)molecules constructs a stereoisogram, which contains two pairs of enantiomers, two pairs of *RS*-diastereomers, and two pairs of holantimers. Such stereoisograms are classified into five types, where the existence of five types has been proven by considering *RS*-stereoisomeric groups [23].

The concept of stereoisograms has first been applied to tetrahedral skeletons, where main targets are organic compounds. A stereoisogram is capable of specifying chirality and *RS*-stereogenicity independently by introducing enantiomeric, *RS*-diastereomeric, and holantimeric relationships [24]. Thereby, *R/S*-stereodescriptors of the Cahn-Ingold-Prelog (CIP) system are clarified to be determined by *RS*-stereogenicity and not by chirality. Then, the *R/S*-stereodescriptors based on the *RS*-stereogenicity are linked to the chirality through chirality faithfulness [25]. Moreover, long-standing unconscious confusion on the terms "prochirality" and "stereogenicity" in the conventional stereochemistry has been revealed and completely settled by means of stereoisograms [19, 26, 27]. Substitution criteria for determining prochirality and pro-*RS*-stereogenicity has been developed on the basis of stereoisograms [28], where pro-*R*/pro-*S*-descriptors are clarified to be specified by *RS*-diastereotopic relationships, not by stereoheterotopic relationships [29]. An advanced concept of *correlation diagrams of stereoisograms* has been proposed to characterize stereoisomers of cyclobutane derivatives [30] as well as binuclear and uninuclear promolecules [31, 32]. More complicated treatments have been necessary to characterize allene derivatives [33–35], ethylene derivatives [36], where point groups, *RS*-

stereoisomeric groups, stereoisomeric groups, and isoskeletal groups are introduced.

As for inorganic complexes, on the other hand, the concept of stereoisograms has been applied to square planar complexes, which are examined by means of point groups, *RS*-stereoisomeric groups, and stereoisomeric groups [37]. On the other hand, stereoisograms of octahedral complexes have not been studied because of complexity due to their high symmetries. Because octahedral complexes play an important role in inorganic chemistry as described above, the next target is to comprehend the stereochemistry of octahedral complexes, which will be examined by means of stereoisograms in the present paper, so as to demonstrate the versatility of stereoisograms in inorganic stereochemistry.

2 *RS*-Stereoisomeric Groups for Octahedral Complexes

2.1 Point Groups for Octahedral Complexes

An octahedral skeleton (**1**) belonging to the point group O_h is selected as a reference skeleton. Its six substitution sites are initially numbered as shown in Fig. 1, where the mode of such reference numbering can be selected arbitrarily without losing generality. In the present article, an octahedron with edges (**1**) is used as an illustration in place of a skeleton diagram with bonds (**1'**) or a square with vertical bonds (**1''**). A reflection operated to **1** generates the corresponding mirror image ($\bar{\mathbf{1}}$), in which the substitution sites are denoted by numbers with an overline in order to show that the correspondence between 1 and $\bar{1}$, between 2 and $\bar{2}$, \dots , or between 6 and $\bar{6}$ stems from the reflection.

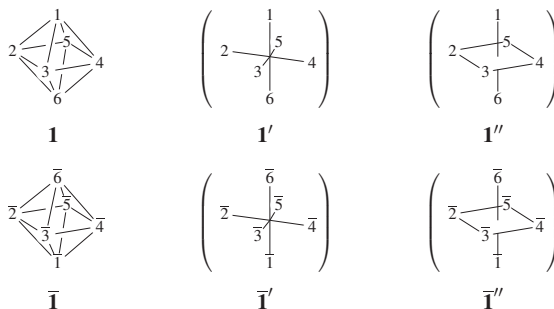


Figure 1: Reference numbering for an octahedral skeleton (**1**) and its mirror image ($\bar{\mathbf{1}}$). The two modes of numbering are enantiomeric to each other.

The elements of the point group O_h are shown in the left part of Fig. 2, which corresponds to the following coset decomposition:

$$O_h = \mathbf{O} + \mathbf{O}i, \quad (1)$$

where the symbol \mathbf{O} represents the point group for indicating the set of 24 rotations for the octahedral skeleton (**1**) and the element i denotes an inversion.

The set of 24 rotations corresponding to the coset \mathbf{O} ($= \mathbf{O}I$) converts the reference octahedral skeleton (**1**) into itself, if the modes of the site numbering are ignored. In other words, the

resulting 24 skeletons with converted modes of numbering are homomeric, where the term *homomeric* is used to denote the equivalence under the group \mathbf{O} .

On the other hand, the coset $\mathbf{O}\bar{i}$ corresponds to the set of 24 roto-reflections to convert the reference octahedral skeleton (**1**) into its mirror images, which are equivalent to each other under the action of \mathbf{O}_h . Or strictly speaking, the resulting 24 skeletons with overlined modes of numbering are homomeric, i.e., equivalent under the action of \mathbf{O} ($= i^{-1}\mathbf{O}i$), so as to generate $\bar{\mathbf{I}}$ as a representative.

The two modes of numbering **1** and $\bar{\mathbf{I}}$ are enantiomeric to each other. Note that the mirror image $\bar{\mathbf{I}}$ is generated on the action of the element $\sigma_{h(1)}$ contained in the coset $\mathbf{O}\bar{i}$, strictly speaking. Each overlined number in $\bar{\mathbf{I}}$ represents the opposite chirality of the corresponding number in **1**, so that the pair of a number and an overlined one can accommodate ligands having opposite chiralities.

According to the unit-subduced-cycle-index (USCI) approach [10], the action of \mathbf{O}_h on the six sites of the octahedral skeleton (**1**) generates an orbit (an equivalence class) governed by a coset representation $\mathbf{O}_h/\langle\mathbf{C}_{4v}\rangle$. The coset representation $\mathbf{O}_h/\langle\mathbf{C}_{4v}\rangle$ consists of permutations which are represented by disjoint cycles collected in Fig. 2, where each overlined permutation represents the changing of the chirality of sites (or ligands accommodated) into the opposite ones. The permutations can be used in place of the elements of the point group \mathbf{O}_h . Note that the point group \mathbf{O}_h (order: $|\mathbf{O}_h| = 48$) represents the global symmetry and its subgroup \mathbf{C}_{4v} (order: $|\mathbf{C}_{4v}| = 8$) represents the local symmetry of each site and that the number 6 of the sites is equal to the degree of the coset representation, as calculated by $|\mathbf{O}_h|/|\mathbf{C}_{4v}| = 48/8 = 6$.

In the present article, octahedral complexes are considered to be derived by placing an appropriate set of ligands or proligands on the six sites of the octahedral skeleton (**1**). The resulting octahedral complexes belong to subgroups of the point group \mathbf{O}_h , as discussed previously [11, 12]. Note that the term *proligand* is used to demonstrate an abstract ligand with chirality/achirality but no 3D-structure [10]. Then an abstract molecule or complex substituted by proligands is called a *promolecule*. The differentiation between ligands and proligands or between molecules and promolecules is not so rigorous in the present article because no serious confusion occurs.

2.2 RS-Permutation Groups and Ligand-Inversion Groups for Octahedral Complexes

Let the symbol \bar{i} be a permutation which is characterized by the same mode of transformation as the permutation corresponding to the inversion i but by no reflection of sites (or ligands accommodated), i.e., $i \sim (1\ 6)(2\ 4)(3\ 5)$, then $\bar{i} \sim (1\ 6)(2\ 4)(3\ 5)$. The multiplication of every elements contained in \mathbf{O} by \bar{i} yields a coset $\mathbf{O}\bar{i}$, the elements of which are collected in the uppright part of Fig. 2. Thereby, we obtain the following group:

$$\mathbf{O}_{\bar{i}} = \mathbf{O} + \mathbf{O}\bar{i}, \quad (2)$$

which is called an *RS-permutation group* or an *RS-stereogenic group*. All of the elements contained in the coset $\mathbf{O}\bar{i}$ convert the reference skeleton (**1**) into a set of skeletons which are equalized under the action of \mathbf{O} (i.e., homomeric). For example, the action of $\tilde{\sigma}_{h(1)} (\in \mathbf{O}\bar{i})$ converts the reference skeleton (**1**) into its *RS*-diastereomer (**2**), where the operation $\tilde{\sigma}_{h(1)}$ is represented by $\tilde{\sigma}_{h(1)} \sim (1\ 6)(2)(3)(4)(5)$. The resulting skeleton **2** is selected as a representative of the set of skeletons corresponding to $\mathbf{O}\bar{i}$. Note that a skeleton derived from any element of $\mathbf{O}\bar{i}$

O	<i>I</i>	(1)(2)(3)(4)(5)(6)	\bar{i}	(1 6)(2 4)(3 5)	O\bar{i}
	<i>C</i> ₂₍₁₎	(1)(2 4)(3 5)(6)	$\bar{\sigma}_{h(3)}$	(1)(2 4)(3)(5)(6)	
	<i>C</i> ₂₍₂₎	(1 6)(3 5)(2)(4)	$\bar{\sigma}_{h(2)}$	(1)(2)(3 5)(4)(6)	
	<i>C</i> ₂₍₃₎	(1 6)(2 4)(3)(5)	$\bar{\sigma}_{h(1)}$	(1 6)(2)(3)(4)(5)	
	<i>C</i> ₃₍₁₎	(1 3 2)(4 6 5)	$\bar{S}_{6(1)}^5$	(1 4 3 6 2 5)	
	<i>C</i> ₃₍₃₎	(1 4 5)(2 3 6)	$\bar{S}_{6(3)}^5$	(1 3 4 6 5 2)	
	<i>C</i> ₃₍₂₎	(1 4 3)(2 5 6)	$\bar{S}_{6(2)}^5$	(1 5 4 6 3 2)	
	<i>C</i> ₃₍₄₎	(1 2 5)(3 6 4)	$\bar{S}_{6(4)}^5$	(1 3 2 6 5 4)	
	<i>C</i> ₃₍₁₎	(1 2 3)(4 5 6)	$\bar{S}_{6(1)}^5$	(1 5 2 6 3 4)	
	<i>C</i> ₃₍₃₎	(1 5 4)(2 6 3)	$\bar{S}_{6(4)}^5$	(1 4 5 6 2 3)	
	<i>C</i> ₃₍₂₎	(1 3 4)(2 6 5)	$\bar{S}_{6(3)}^5$	(1 2 5 6 4 3)	
	<i>C</i> ₃₍₄₎	(1 5 2)(3 4 6)	$\bar{S}_{6(2)}^5$	(1 2 3 6 4 5)	
	<i>C</i> ₂₍₆₎	(1 6)(2 5)(3 4)	$\bar{\sigma}_{d(1)}$	(1)(2 3)(4 5)(6)	
	<i>C</i> ₂₍₁₎	(1 6)(2 3)(4 5)	$\bar{\sigma}_{d(6)}$	(1)(2 5)(3 4)(6)	
	<i>C</i> ₂₍₄₎	(1 2)(3 5)(4 6)	$\bar{\sigma}_{d(2)}$	(1 3)(2)(4)(5 6)	
	<i>C</i> ₂₍₂₎	(1 5)(2 4)(3 6)	$\bar{\sigma}_{d(4)}$	(1 5)(2)(4)(3 6)	
	<i>C</i> ₂₍₅₎	(1 4)(2 6)(3 5)	$\bar{\sigma}_{d(3)}$	(1 4)(2 6)(3)(5)	
	<i>C</i> ₃₍₃₎	(1 3)(2 4)(5 6)	$\bar{\sigma}_{d(5)}$	(1 2)(4 6)(3)(5)	
	<i>C</i> ₄₍₃₎	(1)(2 3 4 5)(6)	$\bar{S}_{4(3)}^3$	(1 6)(2 3 4 5)	
	<i>C</i> ₄₍₃₎	(1)(2 5 4 3)(6)	$\bar{S}_{4(3)}^3$	(1 6)(2 5 4 3)	
	<i>C</i> ₄₍₁₎	(1 5 6 3)(2)(4)	$\bar{S}_{4(1)}^3$	(1 3 6 5)(2 4)	
	<i>C</i> ₄₍₁₎	(1 3 6 5)(2)(4)	$\bar{S}_{4(1)}^3$	(1 5 6 3)(2 4)	
	<i>C</i> ₄₍₂₎	(1 4 6 2)(3)(5)	$\bar{S}_{4(2)}^3$	(1 2 6 4)(3 5)	
	<i>C</i> ₄₍₂₎	(1 2 6 4)(3)(5)	$\bar{S}_{4(2)}^3$	(1 4 6 2)(3 5)	
O\bar{i}	<i>i</i>	(1 6)(2 4)(3 5)	\bar{I}	(1)(2)(3)(4)(5)(6)	O\bar{I}
	$\sigma_{h(3)}$	(1)(2 4)(3)(5)(6)	$\bar{C}_{2(1)}$	(1)(2 4)(3 5)(6)	
	$\sigma_{h(2)}$	(1)(2)(3 5)(4)(6)	$\bar{C}_{2(2)}$	(1 6)(3 5)(2)(4)	
	$\sigma_{h(1)}$	(1 6)(2)(3)(4)(5)	$\bar{C}_{2(3)}$	(1 6)(2 4)(3)(5)	
	$S_{6(1)}^5$	(1 4 3 6 2 5)	$\bar{C}_{3(1)}$	(1 3 2)(4 6 5)	
	$S_{6(3)}^5$	(1 3 4 6 5 2)	$\bar{C}_{3(3)}$	(1 4 5)(2 3 6)	
	$S_{6(2)}^5$	(1 5 4 6 3 2)	$\bar{C}_{3(2)}$	(1 4 3)(2 5 6)	
	$S_{6(4)}^5$	(1 3 2 6 5 4)	$\bar{C}_{3(4)}$	(1 2 5)(3 6 4)	
	$S_{6(1)}$	(1 5 2 6 3 4)	$\bar{C}_{3(1)}^2$	(1 2 3)(4 5 6)	
	$S_{6(4)}$	(1 4 5 6 2 3)	$\bar{C}_{3(3)}^2$	(1 5 4)(2 6 3)	
	$S_{6(3)}$	(1 2 5 6 4 3)	$\bar{C}_{3(2)}^2$	(1 3 4)(2 6 5)	
	$S_{6(2)}$	(1 2 3 6 4 5)	$\bar{C}_{3(4)}^2$	(1 5 2)(3 4 6)	
	$\sigma_{d(1)}$	(1)(2 3)(4 5)(6)	$\bar{C}_{2(6)}^4$	(1 6)(2 5)(3 4)	
	$\sigma_{d(6)}$	(1)(2 5)(3 4)(6)	$\bar{C}_{2(1)}^4$	(1 6)(2 3)(4 5)	
	$\sigma_{d(2)}$	(1 3)(2)(4)(5 6)	$\bar{C}_{2(4)}^4$	(1 2)(3 5)(4 6)	
	$\sigma_{d(4)}$	(1 5)(2)(4)(3 6)	$\bar{C}_{2(2)}^4$	(1 5)(2 4)(3 6)	
	$\sigma_{d(3)}$	(1 4)(2 6)(3)(5)	$\bar{C}_{2(5)}^4$	(1 4)(2 6)(3)(5)	
	$\sigma_{d(5)}$	(1 2)(4 6)(3)(5)	$\bar{C}_{2(3)}^4$	(1 3)(2 4)(5 6)	
	$S_{4(3)}^3$	(1 6)(2 3 4 5)	$\bar{C}_{4(3)}^3$	(1)(2 3 4 5)(6)	
	$S_{4(3)}^3$	(1 6)(2 5 4 3)	$\bar{C}_{4(3)}^3$	(1)(2 5 4 3)(6)	
	$S_{4(1)}^3$	(1 3 6 5)(2 4)	$\bar{C}_{4(1)}^3$	(1 5 6 3)(2)(4)	
	$S_{4(1)}^3$	(1 5 6 3)(2 4)	$\bar{C}_{4(1)}^3$	(1 3 6 5)(2)(4)	
	$S_{4(2)}^3$	(1 2 6 4)(3 5)	$\bar{C}_{4(2)}^3$	(1 4 6 2)(3)(5)	
	$S_{4(2)}^3$	(1 4 6 2)(3 5)	$\bar{C}_{4(2)}^3$	(1 2 6 4)(3)(5)	

Figure 2: *RS*-Stereoisomeric group (**O_{hif}**) for an octahedral skeleton. The elements of the coset **O** (= **O \bar{I}**) are called *rotations*, the elements of the coset **O \bar{i}** are called *rotorefections*, the elements of the coset **O \bar{i}** are called *RS-permutations*, and the elements of the coset **O \bar{I}** are called *ligand reflections*.

can be selected as a representative, because it is homomeric to the counterpart (**3**) by the action of $\tilde{i} \sim (1\ 6)(2\ 4)(3\ 5)$.

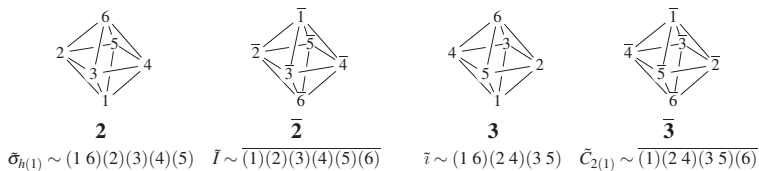


Figure 3: A pair of *RS*-diastereomeric numbering (**2**) and holantimeric numbering ($\bar{\mathbf{2}}$) produced by the actions of $\bar{\sigma}_{h(1)}$ and \bar{I} on the octahedral skeleton (**1**) as well as another pair of *RS*-diastereomeric numbering (**3**) and holantimeric numbering ($\bar{\mathbf{3}}$) produced by the actions of \tilde{i} and $\bar{C}_{2(1)}$ on the octahedral skeleton (**1**). The two pairs are equivalent on the action of **O**. The two modes of numbering for each pair are enantiomeric to each other.

Let the symbol \bar{I} be a permutation which is characterized by the same mode of transformation to the permutation corresponding to the identity I and by reflections of sites (or ligands accommodated). The multiplication of every elements contained in **O** by \bar{I} yields a coset $\mathbf{O}\bar{I}$ collected in the lowerright part of Fig. 2. Thereby, we obtain the following group:

$$\mathbf{O}_{\bar{I}} = \mathbf{O} + \mathbf{O}\bar{I}, \quad (3)$$

which is called a *ligand-inversion group* or a *scleral group*. All of the elements contained in the coset $\mathbf{O}\bar{I}$ convert the reference skeleton (**1**) into a set of skeletons which are equalized under the action of **O**. For example, the action of $\bar{I} (\in \mathbf{O}\bar{I})$ converts the reference skeleton (**1**) into its halantimer ($\bar{\mathbf{2}}$), which is selected as a representative of the set of skeletons corresponding to $\mathbf{O}\bar{I}$. Note that **2** (the *RS*-diastereomer to **1**) and $\bar{\mathbf{2}}$ (the holantimer to **1**) are enantiomeric to each other and that $\bar{\mathbf{1}}$ (the enantiomer to **1**) and $\bar{\mathbf{2}}$ (the enantiomer to **2**) are *RS*-diastereomeric to each other.

2.3 *RS*-Stereoisomeric Groups for Octahedral Complexes

Equations 1, 2, and 3 are combined to give an *RS*-stereoisomeric group represented as follows:

$$\mathbf{O}_{h\bar{i}\bar{I}} = \mathbf{O} + \mathbf{O}i + \mathbf{O}\bar{i} + \mathbf{O}\bar{I}, \quad (4)$$

the elements of which are collected in Fig. 2. The plural form *RS-stereoisomeric groups* is used to designate a set of subgroups of $\mathbf{O}_{h\bar{i}\bar{I}}$, where the group $\mathbf{O}_{h\bar{i}\bar{I}}$ itself is called *the maximum RS-stereoisomeric group* if necessary.

Because the point group **O** is a normal subgroup of the *RS*-stereoisomeric group ($\mathbf{O}_{h\bar{i}\bar{I}}$) (Eq. 4), the four cosets appearing in Eq. 4 generates a factor group of order 4:

$$\mathbf{O}_{h\bar{i}\bar{I}}/\mathbf{O} = \{\mathbf{O}, \mathbf{O}i, \mathbf{O}\bar{i}, \mathbf{O}\bar{I}\}, \quad (5)$$

where the coset **O** plays as an identity element. The factor group $\mathbf{O}_{h\bar{i}\bar{I}}/\mathbf{O}$ is isomorphic to the Klein four-group. Although each derivative of the octahedral skeleton is restricted to belongs to

Table 1: Factor Groups, *RS*-Stereoisomeric Groups, and Types of Stereoisograms

subgroups of the factor group	subgroups of the <i>RS</i> -stereoisomeric group	types of quadruplets	types of stereoisograms
$\{\mathbf{O}\}$	chiral point group \mathbf{O}^a	$\{\mathbf{1}\}, \{\bar{\mathbf{1}}\}, \{\mathbf{2}\}, \{\bar{\mathbf{2}}\}$	Type III
$\{\mathbf{O}, \mathbf{O}\tilde{\mathbf{i}}\}$	<i>RS</i> -permutation group $\mathbf{O}_{\tilde{\mathbf{i}}}$ (Eq. 2) ^{a,b}	$\{\mathbf{1}, \mathbf{2}\}, \{\bar{\mathbf{1}}, \bar{\mathbf{2}}\}$	Type II
$\{\mathbf{O}, \mathbf{O}\tilde{\mathbf{l}}\}$	ligand-inversion group $\mathbf{O}_{\tilde{\mathbf{l}}}$ (Eq. 3) ^a	$\{\mathbf{1}, \bar{\mathbf{2}}\}, \{\bar{\mathbf{1}}, \mathbf{2}\}$	Type I
$\{\mathbf{O}, \mathbf{O}\mathbf{i}\}$	point group \mathbf{O}_h (Eq. 1) ^a	$\{\mathbf{1}, \bar{\mathbf{1}}\}, \{\mathbf{2}, \bar{\mathbf{2}}\}$	Type V
$\{\mathbf{O}, \mathbf{O}\mathbf{i}, \mathbf{O}\tilde{\mathbf{i}}, \mathbf{O}\tilde{\mathbf{l}}\}$	<i>RS</i> -stereoisomeric group $\mathbf{O}_{h\tilde{\mathbf{i}}\tilde{\mathbf{l}}}$ (Eq. 4) ^a	$\{\mathbf{1}, \bar{\mathbf{1}}, \mathbf{2}, \bar{\mathbf{2}}\}$	Type VI

^a Or its subgroups when we consider octahedral derivatives.

^b Or referred to as an *RS*-stereogenic group.

a subgroup of $\mathbf{O}_{h\tilde{\mathbf{i}}\tilde{\mathbf{l}}}$, the factor group corresponding to the subgroup is isomorphic to a subgroup of the factor group $\mathbf{O}_{h\tilde{\mathbf{i}}\tilde{\mathbf{l}}}/\mathbf{O}$ (Eq. 5).

Because the reference skeleton $\mathbf{1}$ corresponds to the coset \mathbf{O} , its enantiomer $\bar{\mathbf{1}}$ corresponds to the coset $\mathbf{O}\mathbf{i}$, its *RS*-diastereomer $\mathbf{2}$ corresponds to the coset $\mathbf{O}\tilde{\mathbf{i}}$, and its halantimer $\bar{\mathbf{2}}$ corresponds to the coset $\mathbf{O}\tilde{\mathbf{l}}$, the factor group $\mathbf{O}_{h\tilde{\mathbf{i}}\tilde{\mathbf{l}}}/\mathbf{O}$ (Eq. 5) characterizes a quadruplet of the *RS*-stereoisomers in a one-to-one fashion:

$$\mathbf{O}_{h\tilde{\mathbf{i}}\tilde{\mathbf{l}}}/\mathbf{O} = \{\mathbf{O}, \mathbf{O}\mathbf{i}, \mathbf{O}\tilde{\mathbf{i}}, \mathbf{O}\tilde{\mathbf{l}}\} \longleftrightarrow \{\mathbf{1}, \bar{\mathbf{1}}, \mathbf{2}, \bar{\mathbf{2}}\} \quad (6)$$

According to a general proof reported in [23], such a factor group $\mathbf{O}_{h\tilde{\mathbf{i}}\tilde{\mathbf{l}}}/\mathbf{O}$ (Eq. 6) has only five subgroups, as shown in Table 1. Each subgroup of the factor group $\mathbf{O}_{h\tilde{\mathbf{i}}\tilde{\mathbf{l}}}/\mathbf{O}$ (Eq. 6) corresponds to a subgroup of the *RS*-stereoisomeric group $\mathbf{O}_{h\tilde{\mathbf{i}}\tilde{\mathbf{l}}}$ (Eq. 4). Note that the *RS*-stereoisomeric group $\mathbf{O}_{h\tilde{\mathbf{i}}\tilde{\mathbf{l}}}$ (Eq. 4) is concerned with a reference octahedral skeleton. It follows that each octahedral derivative exhibits an appropriate subgroup of the *RS*-stereoisomeric group $\mathbf{O}_{h\tilde{\mathbf{i}}\tilde{\mathbf{l}}}$ (Eq. 4). Even to the latter subgroup, the discussions on the basis of factor groups are also effective. Because of the correspondence shown by Eq. 6, quadruplets of *RS*-stereoisomers are categorized into five types, as summarized also in Table 1.

3 Stereoisograms

One of the five subgroups of the factor group $\mathbf{O}_{h\tilde{\mathbf{i}}\tilde{\mathbf{l}}}/\mathbf{O}$ (Eq. 6) characterizes a quadruplet of *RS*-stereoisomers in a one-to-one fashion, as summarized in Table 1. This section is devoted to discuss such quadruplets diagrammatically by means of stereoisograms. Thereby, the stereoisogram approach developed originally to comprehend organic stereochemistry [20–22] is clarified to be effective to inorganic stereochemistry.

3.1 Reference Stereoisogram

As summarized in Fig. 2, the elements of the coset \mathbf{O} ($= \mathbf{O}\mathbf{l}$) are called *rotations*, the elements of the coset $\mathbf{O}\mathbf{i}$ are called *rotorefections*, the elements of the coset $\mathbf{O}\tilde{\mathbf{i}}$ are called *RS-permutations*, and the elements of the coset $\mathbf{O}\tilde{\mathbf{l}}$ are called *ligand reflections*. When these four categories of elements are operated to octahedral derivatives, there appear three types of relationships.

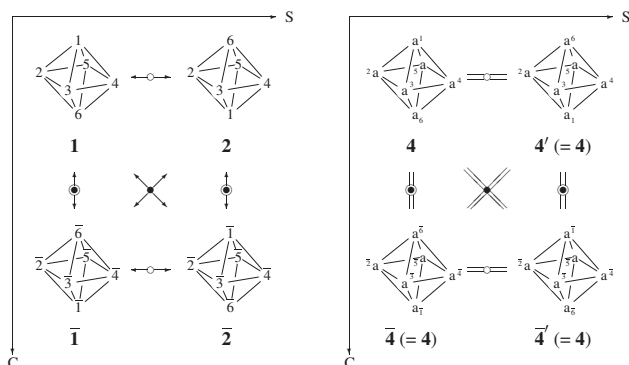


Figure 4: Reference stereoisogram for characterizing an octahedral skeleton (left) and a pro-molecule having the full symmetry of \mathbf{O}_h (right).

Thereby, the resulting *RS*-stereoisomers are characterized by the three types of relationships so as to generate the five types of quadruplets shown in Table 1. As summarized in Table 2, relational terms and symbols have been introduced to characterize the relationships between *RS*-stereoisomers [22] to distinguish the resulting five types of quadruplets (Table 1).

Table 2: Three relationships and the corresponding attributes appearing in stereoisograms [22].

symbol	relationship	attribute
(Concerned with reflections ●)		
↔●	enantiomeric	chiral
↔●=	(self-enantiomeric)	achiral
(Concerned with <i>RS</i> -permutations ○)		
↔○	<i>RS</i> -diastereomeric	<i>RS</i> -stereogenic
↔○=	(self- <i>RS</i> -diastereomeric)	<i>RS</i> -astereogenic
(Concerned with ligand reflections ●)		
↔●	holantimeric	scleral
↔●=	(self-holantimeric)	ascleral

By applying the terminology of Table 2 to the present case, a reference stereoisogram for characterizing a quadruplet of *RS*-stereoisomeric octahedral skeletons (**1**, **1̄**, **2**, and **2̄**) is drawn, as shown in the left of Fig. 4. Note that this stereoisogram is drawn as Type III, tentatively, as discussed later. Six achiral proligands of the same kind (a's) are placed on the sites of the octahedral skeleton to generate the right stereoisogram of Fig. 4, which exhibits the full symmetry of \mathbf{O}_h . Because the mirror image of the achiral proligand coincides with the original proligand, the resulting diagram belongs to Type VI, as discussed later.

3.2 Stereoisograms of Five Types

3.2.1 Stereoisograms of Type I

A stereoisogram of Type I for $(OC-6-43)$ -[Ma₃bcd] is shown as a representative example in the left diagram of Fig. 5, where a, b, c, and d are all achiral prolignands in isolation (when detached), while the letter M represents a central metal atom (omitted). The substitution mode is represented by the following function:

$$f_1 : f_1(1) = a, f_1(2) = a, f_1(3) = a, f_1(4) = c, f_1(5) = d, f_1(6) = b, \quad (7)$$

which is applied to the reference stereoisogram **4** (Fig. 4). A substitution mode other than this mode may be selected without losing generality, so long as the constitution is not changed. The resulting stereoisogram is shown in Fig. 5, where four promolecules are linked by double-headed arrows or equality symbols in accord with Table 2. The promolecules **5** and **5̄** (= **6**) are enantiomeric (the vertical arrows along the C-axis) and *RS*-diastereomeric at the same time (the horizontal arrows along the S-axis), so as to exhibit features of a Type I stereoisogram. The stereoisogram of Type I (Fig. 5) is characterized by chiral, *RS*-stereogenic, and ascleral attributes (stereoisogram index: $[-, -, a]$) according to the terminology summarized in Table 2. The *ascleral* nature corresponds to diagonal equality symbols in the stereoisogram shown in Fig. 5. The stereoisogram index $[-, -, a]$ is composed of prefixes of the attributes, where the symbol $-$ represents no such prefix (e.g., chiral and *RS*-stereogenic in this case) and the symbol *a* represents a prefix of negative meaning (e.g., *ascleral* in this case).

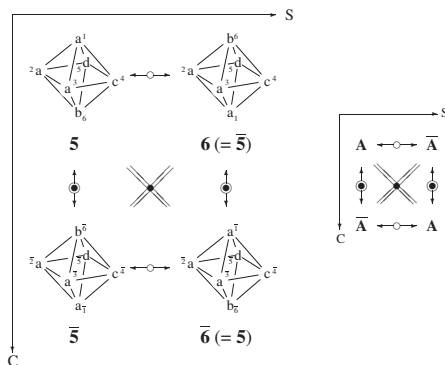


Figure 5: Stereoisogram of Type I for $(OC-6-43)$ -[Ma₃bcd] (left) and the corresponding simplified stereoisogram of Type I (right), where a, b, c, and d are all achiral prolignands in isolation. The CIP priority is presumed to be $a > b > c > d$.

It should be noted that, in the stereoisogram approach, an achiral (pro)ligand 'a' is considered to be transformed into a hypothetical mirror image 'ā' by a (roto)reflection, and then the hypothetical mirror image 'ā' is equalized to the original (pro)ligand 'a', i.e., $\bar{a} = a$. Strictly speaking, hypothetical transformations of this type occur at the six substitution sites of the enantiomer **5̄**. In contrast, they do not occur at the six sites of the *RS*-diastereomer **6**, which is

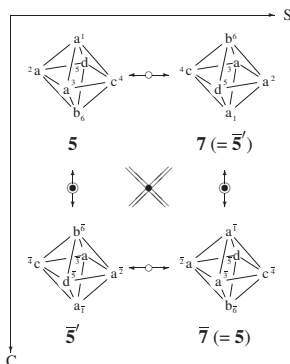


Figure 6: Another representation of the Type I stereoisogram for (OC-6-43)-[Ma₃bcd] (cf. Fig. 5), where a, b, c, and d are all achiral proligands in isolation. The CIP priority is presumed to be a > b > c > d. See the latter mode of numbering shown in Fig. 3.

afterward equalized to $\bar{5}$ because of $\bar{a} = a$. Although these processes appear to be artificial for Type I cases, no notice of them has caused the confusing situations described above for organic and inorganic stereochemistry.

The right diagram of Fig. 5 indicates a simplified stereoisogram of Type I, where \mathbf{A} and $\bar{\mathbf{A}}$ represent a pair of enantiomers. Essential features of the chiral, *RS*-stereogenic, and ascleral nature (stereoisogram index: $[-, -, a]$) can be demonstrated by the simplified stereoisogram of Type I. The asclerality represented by the diagonal equality symbols corresponds to the subgroup $\{\mathbf{O}, \mathbf{O}\bar{I}\}$ or to a subgroup (e.g., $\{I, \bar{I}\}$) of the ligand-inversion group $\mathbf{O}_{\bar{I}}$ (Eq. 3) as shown in Table 1.

Another representation of the stereoisogram of Type I is shown in Fig. 6, where representatives for the *RS*-diastereomer and for an enantiomer are different from those of Fig. 5 (cf. Fig. 3). The $\bar{5}$ of Fig. 5 is homomeric to the $\bar{5}'$ of Fig. 6, where they represent the same chemical entity. Note that the conversion of $\bar{5}$ into the enantiomer $\bar{5}$ in Fig. 5 is brought about by the reflection $\sigma_{h(1)} (= (1\ 6)(2\ 3)(4\ 5))$, while the conversion of $\bar{5}$ into the enantiomer $\bar{5}'$ in Fig. 6 is brought about by the inversion $i (= (1\ 6)(2\ 4)(3\ 5))$. The two stereoisograms of Type I (Figs. 5 and 6) are equivalent under the action of the *RS*-stereoisomeric group $\mathbf{O}_{h\bar{I}\bar{I}}$ (Eq. 4). Although we are able to use either one of these stereoisograms (or other possible stereoisograms), we are mainly use the stereoisogram of Fig. 5, where the numbring of the vertices in Fig. 5 is selected without losing generality.

According to the IR-9.3.3.4 of the IUPAC recommendations 2005 [13], the same configuration index OC-6-43 is assigned to both of the structures ($\bar{5}$ and $\bar{5}$), when the CIP priority sequence is presumed to be a > b > c > d. For the purpose of assuring consistency with stereoisograms of Type III (as described below), this assignment should be considered to be concerned with a pair of the *RS*-diastereomers ($\bar{5}$ and $\bar{6} (= \bar{5})$ along the horizontal S-axis), but not with a pair of enantiomers ($\bar{5}$ and $\bar{5}$ along the vertical C-axis), although the *RS*-diastereomeric pair is superposed onto the enantiomeric pair.

According to the IR-9.3.4.8 of the IUPAC recommendations 2005 [13] but with conceptual

changing, the *C/A*-descriptors (*C* for a clockwise sequence and *A* for an anticlockwise sequence) are given to characterize absolute configurations, i.e.,

$$\left. \begin{array}{ll} OC-6-43-C & \text{for } \mathbf{5} \\ OC-6-43-A & \text{for } \mathbf{6}(=\bar{\mathbf{5}}) \end{array} \right\} \quad (8)$$

which are concerned with the *RS*-diastereomeric relationship between **5** and **6** ($=\bar{\mathbf{5}}$). The provision “with conceptual changing” means that the pair of *C/A*-descriptors is considered not to be given to the pair of enantiomers for the purpose of assuring consistency with stereoisograms of Type III and of Type V (as described below). According to the present stereoisogram approach, the latter descriptor *OC-6-43-A*, which is originally assigned to **6**, is regarded as being reassigned to $\bar{\mathbf{5}}$ (the enantiomer of **5**) in terms of chirality faithfulness [25].

In contrast, the IR-9.3.4.8 of the IUPAC recommendations 2005 [13] is based on the presumption that such *C/A*-descriptors are directly assigned to an enantiomeric pair, e.g., **5** and $\bar{\mathbf{5}}$, because it refers to the *C/A*-descriptors by the name of chirality symbols (*C* and *A*). Strictly speaking, the direct assignment concerned with the pair of enantiomers (**5** and $\bar{\mathbf{5}}$) is permissible only by the equalization of the CIP priority $\bar{a} > \bar{b} > \bar{c} > \bar{d}$ to the CIP priority $a > b > c > d$. This type of equalization is permitted in Type I cases, but not always permitted in Type III cases as discussed later.

We here take account of Fig. 6 in place of Fig. 5 to examine the generality of altering the mode of numbering. This is because the same representatives as used in $\mathbf{O}_{hi\bar{l}}$ (Eq. 4) can be used so as to trace the following discussion more smoothly. Even if Fig. 5 is used, a similar treatment is possible. The structures **5** and $\bar{\mathbf{5}}$ ($=\mathbf{6}$) belong to \mathbf{C}_1 symmetry ($\mathbf{C}_1 \subset \mathbf{O}_h$), geometrically speaking. Hence, the resulting quadruplet is related to the following *RS*-stereoisomeric group:

$$\mathbf{C}_{i\bar{i}\bar{l}} = \mathbf{C}_1 + \mathbf{C}_1\bar{i} + \mathbf{C}_1i + \mathbf{C}_1\bar{l} = \{I, \bar{i}, i, \bar{l}\} \quad (9)$$

which is a subgroup of the maximum *RS*-stereoisomeric group $\mathbf{O}_{hi\bar{l}}$ (Eq. 4). The corresponding factor group is calculated as follows:

$$\mathbf{C}_{i\bar{i}\bar{l}}/\mathbf{C}_1 = \{\mathbf{C}_1, \mathbf{C}_1\bar{i}, \mathbf{C}_1i, \mathbf{C}_1\bar{l}\} = \{I, \bar{i}, i, \bar{l}\}. \quad (10)$$

Hence, its subgroup $\{\mathbf{C}_1, \mathbf{C}_1\bar{l}\} = \{I, \bar{l}\}$ characterizes the stereoisogram of Fig. 5. The factor group $\mathbf{C}_{i\bar{i}\bar{l}}/\mathbf{C}_1$ (Eq. 10) is isomorphic to the factor group $\mathbf{O}_{hi\bar{l}}/\mathbf{O}$ (Eq. 6). In addition, the subgroup $\{\mathbf{C}_1, \mathbf{C}_1\bar{l}\} = \{I, \bar{l}\}$ is isomorphic to the subgroup $\{\mathbf{O}, \mathbf{O}\bar{l}\}$ shown in Table 1. This type of correspondence has been proven in general [23]. It follows that the stereoisogram of Fig. 5 can be discussed by means of the subgroup $\{\mathbf{O}, \mathbf{O}\bar{l}\}$ shown in Table 1.

3.2.2 Stereoisograms of Type II

A stereoisogram of Type II for an enantiomeric pair of (*OC-6-32*)-[Ma₂bcp₂] (**8**) and (*OC-6-32*)-[Ma₂bcp̄₂] ($\bar{\mathbf{8}}$) is shown as a representative example in the left diagram of Fig. 7, where *a*, *b*, and *c* are achiral proligands in isolation, while *p* and \bar{p} represent an enantiomeric pair of chiral proligands in isolation. The substitution mode is represented by the following function:

$$f_2: \quad f_2(1) = a, f_2(2) = a, f_2(3) = p, f_2(4) = c, f_2(5) = p, f_2(6) = b, \quad (11)$$

which is applied to the reference stereoisogram **4** (Fig. 4). The resulting stereoisogram of Type II (Fig. 7, left) is characterized by chiral, *RS*-astereogenic, and scleral attributes (stereoisogram index: $[-, a, -]$) according to the terminology summarized in Table 2.

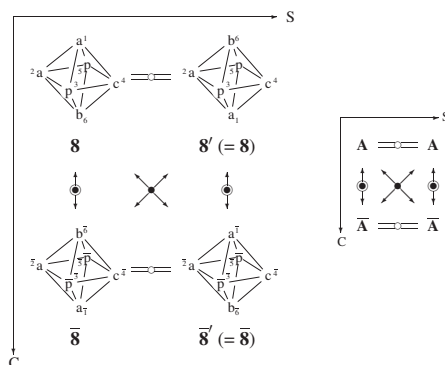


Figure 7: Stereoisogram of Type II for an enantiomeric pair of (*OC*-6-32)-[Ma₂bcp₂] (**8**) and (*OC*-6-32)-[Ma₂bc̄p₂] (**8̄**) (left) as well as the corresponding simplified stereoisogram of Type II (right), where a, b, and c are achiral proligands in isolation, while p and \bar{p} represent an enantiomeric pair of chiral proligands in isolation. The CIP priority: $a > b > c > p$ or $a > b > c > \bar{p}$.

The right diagram of Fig. 7 indicates a simplified stereoisogram of Type II, where **A** and **Ā** represent a pair of enantiomers. Essential features of the chiral, *RS*-astereogenic, and scleral nature (stereoisogram index: $[-, a, -]$) can be demonstrated by the simplified stereoisogram of Type II. The *RS*-astereogenicity is exhibited by the horizontal equality symbols in each of the diagrams of Fig. 7, so that it corresponds to the subgroup **{O, O \bar{r} }** or to a subgroup of the *RS*-permutation group **O \bar{r}** (Eq. 2), as summarized in Table 1.

According to the IR-9.3.3.4 of the IUPAC recommendations 2005 [13] but for the purpose of assuring consistency with stereoisograms of Type III (as described below), the configuration index *OC*-6-32 is assigned to a self-*RS*-diastereomeric pair of **8/8'** (**= 8**) (CIP priority: $a > b > c > p$) or of **8̄/8̄'** (**= 8̄**) (CIP priority: $a > b > c > \bar{p}$). For the purpose of assuring consistency with stereoisograms of Type III (as described below), this assignment for Type II should be also considered to be concerned with each self-*RS*-diastereomeric pair in the present stereoisogram approach. In other words, the configuration index *OC*-6-32 for **8** is independent to the configuration index *OC*-6-32 for **8̄**.

C/A-Descriptors cannot be given to the octahedral centers of the enantiomeric pair of **8/8̄** by virtue of the IR-9.3.4.8 of the IUPAC recommendations 2005 [13]. This means that such *C/A*-descriptors are not concerned with such chirality as differentiating the enantiomers **8** and **8̄**. In other words, the presumption that *C/A*-descriptors are concerned with chirality so as to be assigned directly to an enantiomeric pair (as implied in the IR-9.3.4.8 of the IUPAC recommendations 2005 [13]) loses its theoretical basis.

The conventional stereochemistry is silent on the reason of the incapability of giving *C/A*-descriptors. Although the ligands p and \bar{p} are named by *RS*-descriptors in order to differentiate the enantiomers **8** and **8̄**, the enantiomeric relationship between them is not clearly demonstrated by such indirect differentiation. According to the present stereoisogram approach, in contrast, the incapability is ascribed to the *RS*-astereogenic nature of the stereoisogram of Type

II, which contains relevant structures **8** and $\bar{\mathbf{8}}$ as a quadruplet of *RS*-stereoisomers.

Stereoisograms of Type II provide us with counterexamples to such an erroneous statement as “Stereogenic centers may, or may not be centers of chirality, but all chiral centers are stereogenic.”, which appears, for example, in a textbook of inorganic stereochemistry (page 58 of [5]) as well as of organic stereochemistry (page 33 of [38]). Note that the center (the central metal atom) of **8** is chiral geometrically because it is the mirror image of the center of $\bar{\mathbf{8}}$. However, these centers are not *RS*-stereogenic in terms of the stereoisogram approach (Type II), and not stereogenic in terms of the conventional stereochemistry. Hence, the second half of the above statement “all chiral centers are stereogenic.” does not hold true for the Type II case. This inconsistency of the conventional stereochemistry has been discussed in detail in Section 10.2.1 of [19].

Geometrically speaking, the structures **8** and $\bar{\mathbf{8}}$ belong to C_1 symmetry ($C_1 \subset O_h$). Hence, the resulting quadruplet is related to the following *RS*-stereoisomeric group:

$$C_{h\tilde{\sigma}_h\tilde{I}} = C_1 + C_1\tilde{\sigma}_{h(1)} + C_1\sigma_{h(1)} + C_1\tilde{I} = \{I, \tilde{\sigma}_{h(1)}, \sigma_{h(1)}, \tilde{I}\} \quad (12)$$

which is a subgroup of the maximum *RS*-stereoisomeric group $O_{h\tilde{I}}$ (Eq. 4). The corresponding factor group is calculated as follows:

$$C_{h\tilde{\sigma}_h\tilde{I}}/C_1 = \{C_1, C_1\tilde{\sigma}_{h(1)}, C_1\sigma_{h(1)}, C_1\tilde{I}\} = \{I, \tilde{\sigma}_{h(1)}, \sigma_{h(1)}, \tilde{I}\}. \quad (13)$$

Hence, its subgroup $\{C_1, C_1\tilde{\sigma}_{h(1)}\} = \{I, \tilde{\sigma}_{h(1)}\}$ characterizes the stereoisogram of Fig. 7. The factor group $C_{h\tilde{\sigma}_h\tilde{I}}/C_1$ is isomorphic to the factor group $O_{h\tilde{I}}/O$ (Eq. 6). In addition, the subgroup $\{C_1, C_1\tilde{\sigma}_{h(1)}\} = \{I, \tilde{\sigma}_{h(1)}\}$ is isomorphic to the subgroup $\{O, O\tilde{\sigma}\}$ shown in Table 1. This type of correspondence has been proven in general [23]. It follows that the stereoisogram of Fig. 7 can be discussed by means of the subgroup $\{O, O\tilde{\sigma}\}$ shown in Table 1.

3.2.3 Stereoisograms of Type III

A stereoisogram of Type III for (*OC*-6-52)- and (*OC*-6-42)-[Ma₂bcp \bar{p}] is shown in the left diagram of Fig. 8, where a, b, and c are achiral proligands in isolation, while p and \bar{p} represent an enantiomeric pair of chiral proligands in isolation. The substitution mode is represented by the following function:

$$f_3: \quad f_3(1) = a, f_3(2) = a, f_3(3) = c, f_3(4) = \bar{p}, f_3(5) = p, f_3(6) = b, \quad (14)$$

which is applied to the reference stereoisogram **4** (Fig. 4). The stereoisogram of Type III is characterized by chiral, *RS*-stereogenic, and scleral attributes (stereoisogram index: $[-, -, -]$) according to the terminology summarized in Table 2.

The right diagram of Fig. 8 indicates a simplified stereoisogram of Type III, where **A** and $\bar{\mathbf{A}}$ as well as **B** and $\bar{\mathbf{B}}$ represent pairs of enantiomers. The simplified stereoisogram of Type III is capable of showing essential features of the chiral, *RS*-stereogenic, and scleral nature (stereoisogram index: $[-, -, -]$). The absence of equality symbols characterizes each of the diagrams of Fig. 8, so that the Type III case corresponds to the factor subgroup $\{O\}$ or to a subgroup of the chiral point group **O**, as summarized in Table 1.

According to the IR-9.3.3.4 of the IUPAC recommendations 2005 [13], the configuration index *OC*-6-52 is assigned to a pair of *RS*-diastereomers **9/10**, while the configuration index *OC*-6-42 is assigned to another pair of *RS*-diastereomers $\bar{\mathbf{9}}/\bar{\mathbf{10}}$. It should be noted that an enantiomeric pair of **9/9** (or another enantiomeric pair of **10/10**) corresponds to different configuration indices, i.e., *OC*-6-52 and *OC*-6-42.

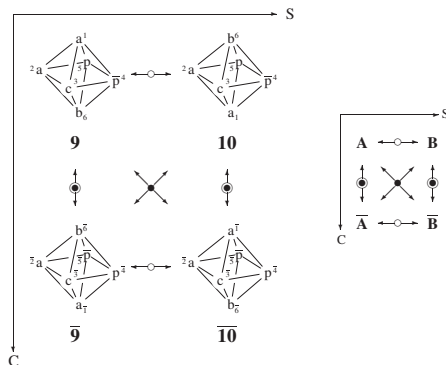


Figure 8: Stereoisogram of Type III for [Ma₂bcp̄p̄] (left) and the corresponding simplified stereoisogram of Type III (right), where a, b, and c are achiral proligands in isolation, while p and p̄ represent an enantiomeric pair of chiral proligands in isolation. The CIP priority: a > b > c > p > p̄.

When the CIP priority sequence is presumed to be a > b > c > p > p̄, the *C/A*-descriptors of respective promolecules are assigned as follows:

$$\left. \begin{array}{ll} OC-6-52-C & \text{for } \mathbf{9} \\ OC-6-52-A & \text{for } \mathbf{10} \\ OC-6-42-A & \text{for } \mathbf{\bar{9}} \\ OC-6-42-C & \text{for } \mathbf{\bar{10}} \end{array} \right\} \quad (15)$$

according to the IR-9.3.4.8 of the IUPAC recommendations 2005 [13]. Obviously, *OC-6-52-C* and *OC-6-52-A* are pairwise assigned to a relevant pair of *RS*-diastereomers (**9** and **10**), while *OC-6-42-A* and *OC-6-42-C* are pairwise assigned to another relevant pair of *RS*-diastereomers (**9̄** and **10̄**). It should be noted the symbol *C* (clockwise sequence: a → c → b → p) of *OC-6-52-C* is not paired with the symbol *A* (anticlockwise sequence: a → c → b → p̄) of *OC-6-42-A*, where such an unpaired feature causes the difference between the configuration indices, *OC-6-52* and *OC-6-42*. In a similar way, the symbol *A* (anticlockwise sequence: a → c → b → p) of *OC-6-52-A* is not paired with the symbol *C* (clockwise sequence: a → c → b → p̄) of *OC-6-42-C*. As a result, a pair of *A*- and *C*-descriptors is concluded to be given to a pair of *RS*-diastereomers, but not to a pair of enantiomers. Although the symbols *A* and *C* are originally called “chirality symbols” in the IUPAC recommendations 2005 [13], the naming is inadequate and they should be called “*RS*-stereogenicity symbols”.

If *C/A*-descriptors are used to refer to a pair of enantiomers, the concept of chirality faithfulness [25] should be taken into consideration, as discussed later.

Geometrically speaking, the promolecules **9** etc. belong to **C**₁ symmetry (**C**₁ ⊂ **O**_{*h*}). Hence, the resulting quadruplet belongs to the *RS*-stereoisomeric group represented by Eq. 12. Hence, the subgroup {**C**₁} = {*I*} of the factor group (Eq. 13) characterizes the stereoisogram of Fig. 8. It follows that the stereoisogram of Fig. 8 can be discussed by means of the subgroup {**O**} of the factor group **O**_{*h*}**I**/**O** (Eq. 6), as shown in Table 1.

3.2.4 Stereoisograms of Type IV

A stereoisogram of Type IV for (*OC-6-4I*)-[Ma₃bcd] is shown in the left diagram of Fig. 9, where a, b, c, and d are achiral proligands in isolation. The mode of substitution is represented by the following function:

$$f_4 : f_4(1) = a, f_4(2) = a, f_4(3) = c, f_4(4) = d, f_4(5) = b, f_4(6) = a, \quad (16)$$

which is applied to the reference stereoisogram **4** (Fig. 4). The stereoisogram of Type IV (Fig. 9, left) is an extreme case in which four relevant *RS*-stereoisomers are degenerated into a single promolecule, so as to be characterized by achiral, *RS*-astereogenic, and ascleral attributes (stereoisogram index: [*a, a, a*]) according to the terminology summarized in Table 2.

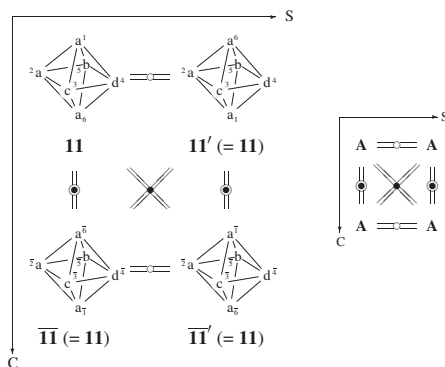


Figure 9: Stereoisogram of Type IV for (*OC-6-4I*)-[Ma₃bcd] (left) and the corresponding simplified stereoisogram of Type IV (right), where a, b, c, and d are all achiral proligands in isolation. The CIP priority: *a* > *b* > *c* > *d*.

The right diagram of Fig. 9 indicates a simplified stereoisogram of Type IV, which contains a single molecule **A**. The simplified stereoisogram of Type IV is capable of showing essential features of the achiral, *RS*-astereogenic, and ascleral nature (stereoisogram index: [*a, a, a*]). The total features of the Type IV case correspond to the subgroup {**O**, **O_i**, **O_r**, **O_l**} (the factor group itself) or to a subgroup of the *RS*-stereoisomeric group **O_hl̄** (Eq. 4), as shown in Table 1.

According to the IR-9.3.3.4 of the IUPAC recommendations 2005 [13], the configuration index *OC-6-4I* is assigned to **11**, which requires no *C/A*-descriptors.

Geometrically speaking, the structures **11** belongs to **C_s** symmetry (**C_s** = **C₁** + **C₁σ_{h(1)}** ⊂ **O_h**), so that the *RS*-stereoisomeric group represented by Eq. 12 is taken into consideration. The corresponding factor group is represented by Eq. 13, which characterize the Type IV stereoisogram of Fig. 9. The factor group (Eq. 13) is isomorphic to the factor group **O_hl̄**/**O** (Eq. 6). It follows that the stereoisogram of Fig. 9 can be discussed by means of the factor group **O_hl̄**/**O** (Eq. 6) shown in Table 1.

3.2.5 Stereoisograms of Type V

A stereoisogram of Type V for $(OC-6-32)$ -[Ma₂bcp \bar{p}] is shown in the left diagram of Fig. 10, where a, b, and c are achiral proligands in isolation, while p and \bar{p} represent an enantiomeric pair of chiral proligands in isolation. The mode of substitution is represented by the following function:

$$f_5: \quad f_5(1) = a, f_5(2) = a, f_5(3) = \bar{p}, f_5(4) = c, f_5(5) = p, f_5(6) = b, \quad (17)$$

which is applied to the reference stereoisogram **4** (Fig. 4). The stereoisogram of Type V (Fig. 10, left) is characterized by achiral, *RS*-stereogenic, and scleral attributes (stereoisogram index: $[a, -, -]$) according to the terminology summarized in Table 2. The achirality is expressed by the vertical equality symbols in the left diagram of Fig. 10. The configuration index *OC*-6-32 is assigned to a pair of *RS*-diastereomers **12/13** according to the IR-9.3.3.4 of the IUPAC recommendations 2005 [13].

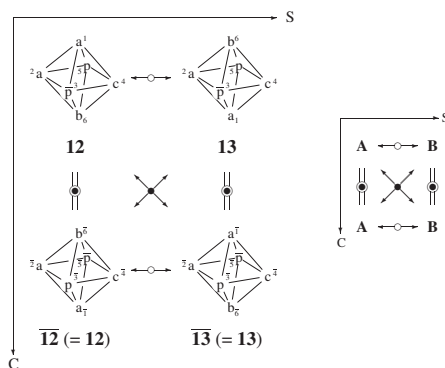


Figure 10: Stereoisogram of Type V for $(OC-6-32)$ -[Ma₂bcp \bar{p}] (left) and the corresponding simplified stereoisogram of Type V (right), where a, b, and c are achiral proligands in isolation, while p and \bar{p} represent an enantiomeric pair of chiral proligands in isolation. The CIP priority: $a > b > c > p > \bar{p}$.

The corresponding simplified stereoisogram of Type V shown in the right diagram of Fig. 10 is capable of showing essential features of the achiral, *RS*-stereogenic, and scleral nature (stereoisogram index: $[a, -, -]$). Thereby achiral molecules **A** and **B** are concluded to be *RS*-diastereomeric so that they exhibit an extended feature of pseudoasymmetry. The Type V case corresponds to the subgroup $\{\mathbf{O}, \mathbf{O}_i\}$ or to a subgroup of the point group \mathbf{O}_h (Eq. 1), as summarized in Table 1.

Although the two molecules **12** and **13** are achiral, *C/A*-descriptors can be assigned to them, when the priority sequence is presumed to be $a > b > c > p > \bar{p}$. Thus, the *C/A*-descriptor of each promolecule is assigned as follows:

$$\left. \begin{array}{ll} OC-6-32-A & \text{for } \mathbf{12} \\ OC-6-32-C & \text{for } \mathbf{13} \end{array} \right\} \quad (18)$$

according to the IR-9.3.4.8 of the IUPAC recommendations 2005 [13]. The stereoisogram of Type V (Fig. 10) indicates that pairwise *C/A*-descriptors are given to an *RS*-diastereomeric pair, not to an enantiomeric pair, because of the absence of enantiomeric pairs.

Geometrically speaking, the structures **12** and **13** belong to C_s symmetry ($C_s = C_1 + C_1\sigma_{h(2)} \subset O_h$). Hence, the resulting quadruplet is characterized by the following *RS*-stereoisomeric group:

$$C'_{h\tilde{\sigma}_h\tilde{I}} = C_1 + C_1\tilde{\sigma}_{h(2)} + C_1\sigma_{h(2)} + C_1\tilde{I} = \{I, \tilde{\sigma}_{h(2)}, \sigma_{h(2)}, \tilde{I}\} \quad (19)$$

which is a subgroup of the maximum *RS*-stereoisomeric group $O_{h\tilde{I}\tilde{I}}$ (Eq. 4). The corresponding factor group is calculated as follows:

$$C'_{h\tilde{\sigma}_h\tilde{I}}/C_1 = \{C_1, C_1\tilde{\sigma}_{h(2)}, C_1\sigma_{h(2)}, C_1\tilde{I}\} = \{I, \tilde{\sigma}_{h(2)}, \sigma_{h(2)}, \tilde{I}\}. \quad (20)$$

Hence, its subgroup $\{C_1, C_1\sigma_{h(2)}\} = \{I, \sigma_{h(2)}\}$ characterizes the stereoisogram of Fig. 10. The factor group $C'_{h\tilde{\sigma}_h\tilde{I}}/C_1$ is isomorphic to the factor group $O_{h\tilde{I}\tilde{I}}/O$ (Eq. 6). In addition, the subgroup $\{C_1, C_1\sigma_{h(2)}\} = \{I, \sigma_{h(2)}\}$ is isomorphic to the subgroup $\{O, Oi\}$ shown in Table 1. It follows that the stereoisogram of Fig. 10 can be discussed by means of the subgroup $\{O, Oi\}$ shown in Table 1.

4 Chirality and *RS*-Stereogenicity

4.1 Summary of Stereoisograms of Five Types

As found in the constructions of the *RS*-stereoisomeric group ($O_{h\tilde{I}\tilde{I}}$ of Eq. 4) and of the corresponding factor group ($O_{h\tilde{I}\tilde{I}}/O$ of Eq. 5) by starting from the point group O_h , the factor group ($O_{h\tilde{I}\tilde{I}}/O$ of Eq. 5) is isomorphic to factor groups which have been discussed generally by starting from appropriate point groups other than O_h [23]. Hence, the scheme of simplified stereoisograms reported in the general discussion [22] is also effective to the present cases based on O_h , as cited in Fig. 11. Note that the term *ligand* is originally defined as “the atoms or groups joined to the central atom in an inorganic coordination entity” in inorganic terminology. In the stereoisogram approach, the term *ligand* is also used to refer to atoms and groups which are regarded as substituents in organic chemistry, so that such an extended usage provides us with a common theoretical basis to stereochemistry, both organic and inorganic.

According to the simplified stereoisograms summarized in Fig. 11, the following features of the respective types should be mentioned:

1. a quadruplet of *RS*-stereoisomers assigned to a stereoisogram of Type I is regarded as being degenerated into a pair of enantiomers,
2. a quadruplet of *RS*-stereoisomers assigned to a stereoisogram of Type II is regarded as being degenerated into a pair of enantiomers,
3. a quadruplet of *RS*-stereoisomers assigned to a stereoisogram of Type III is regarded as retaining the full feature so as to have two pairs of enantiomers,
4. a quadruplet of *RS*-stereoisomers assigned to a stereoisogram of Type IV is regarded as being degenerated into a single achiral compound, and
5. a quadruplet of *RS*-stereoisomers assigned to a stereoisogram of Type V is regarded as being degenerated into a pair of *RS*-diastereomers.

	<i>RS</i> -astereogenic	<i>RS</i> -stereogenic
chiral		<p>Type I: $[-, -, a]$ chiral/ <i>RS</i>-stereogenic/ ascleral</p>
	<p>Type II: $[-, a, -]$ chiral/ <i>RS</i>-astereogenic/ scleral</p>	<p>Type III: $[-, -, -]$ chiral/ <i>RS</i>-stereogenic/ scleral</p>
achiral	<p>Type IV: $[a, a, a]$ achiral/ <i>RS</i>-astereogenic/ ascleral</p>	<p>Type V: $[a, -, -]$ achiral/ <i>RS</i>-stereogenic/ scleral</p>

Figure 11: Stereoisograms of five types [22]. The symbols **A** and $\overline{\mathbf{A}}$ (or **B** and $\overline{\mathbf{B}}$) represent a pair of enantiomers.

If only achiral ligands are considered to be substituents (just as the conventional stereochemistry has postulated frequently [16, 17]), there appear Type I and IV cases only. This means that we are forced to take main account of Type I and IV cases, so that cases assigned to stereoisograms of Type V are considered to be exceptional cases by naming them “pseudoasymmetry” and Type II and III cases are ignored unconsciously. The deficiency of Types II and III along with the exceptional treatment of Type V has brought about confusions to the conventional stereochemistry, as implied in various ways by reviews [39, 40, 41].

However, no essential solutions to the confusions have appeared in the conventional stereochemistry because Types II and III are by no means deduced without the concept of stereoisograms. Moreover, it should be emphasized that there is no common basis for rationalizing such a pair of enantiomers for Type I cases and such a pair of *RS*-diastereomers for Type V cases, so long as we are restricted to the conventional stereochemistry. In contrast, the stereoisogram approach provides us with an integrated basis to discuss the pairs of the two different categories in the form of *RS*-stereoisomers, as discussed for organic stereochemistry [19, 20, 42] as well as for inorganic stereochemistry in the present article.

4.2 Chirality for Characterizing Enantiomers

In the conventional stereochemistry, the terms “absolute configurations” and “*C/A*-descriptors” (or “*R/S*-descriptors” in organic stereochemistry) have been directly linked to chirality or enantiomers, as implied by the section title “Describing absolute configuration—distinguishing between enantiomers” (Section IR-9.3.4) and by the terminology such as “chirality symbols” for referring to *C/A*-descriptors in the IUPAC recommendations 2005 [13].

As summarized in Fig. 11, however, chiral promolecules are categorized into Type I, II, or III, among which absolute configurations are concerned with the centers of Type I and III. The centers of Type II (concerning chiral promolecules) are not characterized by specifying absolute configurations. Moreover, the centers of Type V (concerning achiral promolecules) are characterized by specifying absolute configurations, where their achiralities indicate the absence of enantiomers. It follows that the term “absolute configurations” is by no means a direct specification of chirality or enantiomeric relationships. As a result, *C/A*-descriptors for describing absolute configurations are not directly concerned with chirality or enantiomeric relationships.

Because the conventional stereochemistry lacks such categorization into Types I–V, these have not been properly treated. Thus, the term “absolute configuration” has been used to refer to Type I cases as an apparent remedy, so that Type V cases are treated as exceptional cases (“pseudoasymmetry”) because of achirality and Type II cases are ignored though chiral. This apparent remedy has caused such confused situations as described in the Introduction.

The discussions in the preceding paragraphs mean that the concept of *absolute configurations* is concerned with promolecules of Type I, III, and V, the common attribute of which is found to be *RS*-stereogenicity. As a result, *C/A*-descriptors should be linked to *RS*-stereogenicity or *RS*-diastereomers in terms of the stereoisogram approach. Hence, the section title should be corrected to be “Describing absolute configuration—distinguishing between *RS*-diastereomers” as well as the term “chirality symbols” should be corrected to be “*RS*-stereogenicity symbols”.

By referring to stereoisograms of Types I–V, chirality is judged by examining their vertical *C*-axes (chirality axes), which characterize chirality/achirality or enantiomeric/self-enantiomeric relationships. It should be emphasized that chirality is an independent concept to *RS*-stereogenicity, which provides a basis of examining absolute configurations and of giving *C/A*-descriptors.

This point of emphasis will be further discussed in the following subsections.


4.3 *RS*-Stereogenicity for Giving *C/A*-Descriptors

4.3.1 Single Criterion in the Stereoisogram Approach

As summarized in Table 2, chirality/achirality and *RS*-stereogenicity/*RS*-astereogenicity are independent concepts. The discussions on Types I–V (Figs. 5–10) have revealed that the capability of naming *C/A*-descriptors is ascribed to *RS*-stereogenicity (stereoisograms of Type I, III, and V), but not to chirality (stereoisograms of Type I, II, and III). In other words, *C/A*-descriptors are pairwise assigned to a pair of *RS*-diastereomers, but not to a pair of enantiomers. The capability of naming *C/A*-descriptors is summarized as a single criterion shown in Table 3. This criterion for giving *C/A*-descriptors in inorganic chemistry is consistent with the single criterion for giving *R/S*-descriptors in organic chemistry (cf. Table 10.2 of [19]).

Table 3: Single Criterion for Giving *C/A*-Descriptors in the Stereoisogram Approach.

	chirality	<i>RS</i> -stereogenicity
Type I	enantiomeric	<i>RS</i> -diastereomeric
Type III	enantiomeric	<i>RS</i> -diastereomeric
Type V	self-enantiomeric	<i>RS</i> -diastereomeric


 (chirality-faithfulness)

In particular, Type I cases are contrary to the conventional stereochemistry. Because the conventional stereochemistry lacks *RS*-diastereomeric relationships as pairwise relationships, enantiomeric relationships are considered to be pairwise relationships in the Type I cases so that a pair of *C/A*-descriptors is presumed to be given to a pair of enantiomers. As explained for the Type I stereoisogram of Fig. 5, the *C*-descriptor in *OC*-6-32-*C* assigned to **5** is paired with the *A*-descriptor in *OC*-6-32-*A* assigned to **6** (= **5**), where **5** and **6** are regarded as being *RS*-diastereomeric. Although they are also enantiomeric, the enantiomeric relationships are concluded to be incapable of such pairwise naming by comparing the Type I case with Type V (or III).

For example, if *C/A*-descriptors are pairwise assigned to a pair of enantiomers, the pairwise naming of Type V (cf. Fig. 10) would be impossible because **12** (as well as **13**) is achiral, i.e., enantiomeric pairs are absent. However, the *C/A*-descriptors in *OC*-6-32-*A* for **12** and *OC*-6-32-*C* for **13** can be given so as to be paired in accord with the *RS*-diastereomeric relationship between **12** and **13**.

The stereoisogram of Type III indicates the coexistence of enantiomeric relationships and *RS*-diastereomeric relationships, where the *RS*-diastereomeric relationships are clues for giving *C/A*-descriptors. For example, the stereoisogram shown in Fig. 8 gives *C/A*-descriptors shown in Eq. 15, where a pair of *C/A*-descriptors (*OC*-6-52-*C/OC*-6-52-*A*) is considered to be given to a pair of *RS*-diastereomers (**9/10**) as well as another pair of *C/A*-descriptors (*OC*-6-42-*A/OC*-6-42-*C*) is considered to be given to a pair of *RS*-diastereomers (**9/10**).

4.3.2 Entangled Criteria in the Conventional Stereochemistry

If we obey the conventional stereochemistry in which the concept of *RS*-stereogenicity is absent, we are forced to use the following criteria:

1. As for the Type I stereoisogram of Fig. 5, the *C*-descriptor in *OC*-6-32-*C* assigned to **5** is considered to be paired with the *A*-descriptor in *OC*-6-32-*A* assigned to enantiomer **5̄**.
2. Because of the absence of enantiomeric relationships for Type V cases (e.g., **12** and **13**), the conventional stereochemistry is forced to presume that a pair of *C/A*-descriptors is given to a pair of diastereomers, although such pairing of diastereomers is not fully formulated so long as we obey the conventional stereochemistry.
3. As for the Type III case of Fig. 8 (Eq. 15), the conventional stereochemistry adopts one pair *OC*-6-52-*C/OC*-6-42-*A* for the enantiomeric pair **9/9̄** and the other pair *OC*-6-52-*A/OC*-6-42-*C* for the enantiomeric pair **10/10̄**, because the terminology of the conventional stereochemistry lacks *RS*-diastereomeric relationships as pairwise relationships. Thus, this case indicates a seeming example in which enantiomeric relationships are used as a clue for giving *C/A*-descriptors. However, the configuration indices in each pair are not identical, whereas the *C/A*-descriptors are regarded as being paired if we obey the conventional stereochemistry.

The above-mentioned criteria for giving *C/A*-descriptors in the conventional stereochemistry are entangled, as summarized in Table 4. The entangled criteria for giving *C/A*-descriptors succeed the entangled criteria for giving *R/S*-descriptors in organic chemistry (cf. Table 10.3 of [19]). These criteria should be replaced by the single criterion shown in Table 3.

Table 4: Entangled Criteria to be Abandoned in the Conventional Approach for Giving *C/A*-Descriptors

	chirality	(\subset stereogenicity)
Type I	"enantiomeric"	–
Type III	"enantiomeric"	"diastereomeric"
Type V	–	"diastereomeric"
	"chirality units"	"pseudoasymmetric units"
	<div style="text-align: center;"> $\underbrace{\hspace{10em}}$ "stereogenic units" </div>	

Another seemingly irregular case of Type III should be added here, because it requires the entangled criteria shown in Table 4 if we obey the conventional stereochemistry. Suppose that four achiral ligands (2a and b), an enantiomeric pair of chiral ligands (*p* and *p̄*), and a chiral ligand (*q* or *q̄*) are placed on the six vertices of the reference octahedron skeleton **2**, where the substitution mode is represented by the following function:

$$f_6: \quad f_6(1) = a, f_6(2) = a, f_6(3) = p, f_6(4) = q, f_6(5) = \bar{p}, f_6(6) = b. \quad (21)$$

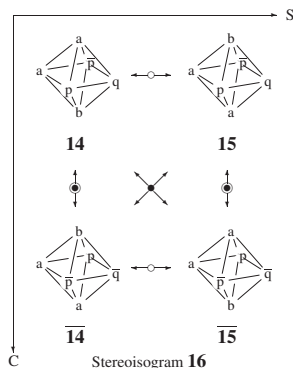


Figure 12: Stereoisogram of Type III for exemplifying a chirality-unfaithful case. The CIP priority: $a > b > p > \bar{p} > q > \bar{q}$.

This function is applied to the 15 reference stereoisograms. Among the resulting *RS*-stereoisomers, let us examine an *RS*-stereoisomer of Type III, the stereoisogram (**16**) of which is shown in Fig. 12.

When the CIP priority $a > b > p > \bar{p} > q > \bar{q}$ is presumed and applied to each promolecules contained in the stereoisogram **16**, the following configuration indices and *C/A*-descriptors are decided:

$$\left. \begin{array}{l} \mathbf{14} \quad OC-6-52-C \\ \mathbf{15} \quad OC-6-52-A \\ \overline{\mathbf{14}} \quad OC-6-62-C \\ \overline{\mathbf{15}} \quad OC-6-62-A \end{array} \right\} \left. \vphantom{\begin{array}{l} \mathbf{14} \\ \mathbf{15} \\ \overline{\mathbf{14}} \\ \overline{\mathbf{15}} \end{array}} \right\} (C_1) \quad \text{Stereoisogram } \mathbf{16} \text{ (Type III)} \quad (22)$$

According to the single criterion shown in Table 3, a pair of *C/A*-descriptors (*OC-6-52-C/OC-6-52-A*) is considered to be given to a pair of *RS*-diastereomers (**14/15**) as well as another pair of *C/A*-descriptors (*OC-6-62-C/OC-6-62-A*) is considered to be given to a pair of *RS*-diastereomers (**14/15**).

From a conventional viewpoint on the other hand, Eq. 22 seemingly shows that an enantiomeric pair of **14/14** is linked to a pair of *OC-6-52-C/OC-6-62-C* and that an enantiomeric pair of **15/15** is linked to a pair of *OC-6-52-A/OC-6-62-A*. Thus, the *A*-descriptor is not paired with the *C*-descriptor in each of these assignments, so that these assignments are contrary to the conventional stereochemistry which is presumed to give a pair of *C/A*-descriptors to a pair of enantiomers. The conventional stereochemistry seems to make little of this type of inconsistency, where it unconsciously ignores the pairwise nature of *C/A*-descriptors (or *R/S*-descriptors) even though it provides a remedy by introducing the term “reflection-invariant descriptors” [43]. To avoid this drawback without ignoring the pairwise nature of *C/A*-descriptors, the entangled criteria summarised in Table 4 are required if we maintain the conventional stereochemistry. Thus, Eq. 15 requires enantiomeric relationships, while Eq. 22 requires diastereomeric relationships according to Table 4. It should be emphasized, moreover, that the diastereomeric relationships

of the conventional stereochemistry are not pairwise relationships, so as to be incapable of asuring the pairwise nature of *C/A*-descriptors even if the entangled criteria (Table 4) are taken into consideration. It follows that such entangle criteria should be abandoned and replaced by the single criterion shown in Table 3.

4.3.3 Chirality Faithfulness

As implied by the section title “Describing absolute configuration — distinguishing between enantiomers” of the IR-9.3.4 of the IUPAC recommendations 2005 [13], *C/A*-descriptors for describing absolute configurations are assigned directly to enantiomers (chirality) in the conventional stereochemistry. More precisely speaking, enantiomeric relationships of the conventional stereochemistry are directly used as one of entangled criteria in the assignment of *C/A*-descriptors (cf. Table 4).

However, the stereoisogram approach of the present article has revealed that *C/A*-descriptors are assigned to *RS*-diastereomers (*RS*-stereogenicity) in terms of the single criterion summarized in Table 3. Such *C/A*-descriptors as assigned first to *RS*-diastereomers (cf. Table 3) are afterward interpreted to be linked to enantiomers, where there appears faithful or unfaithful linkage, as discussed in terms of *chirality faithfulness* [25]. Thereby, the present stereoisogram approach is harmonized with the conventional stereochemistry.

The previous discussion on organic stereochemistry [25] is effective to inorganic stereochemistry. Among three *RS*-stereogenic types (Type I, III, and V), the chirality faithfulness demonstrates the following cases by referring to respective stereoisograms:

1. A stereoisogram of Type I shows that a pair of *C/A*-descriptors given to a pair of *RS*-diastereomers can be interpreted as being given to a pair of enantiomers, because enantiomeric relationships coincide with *RS*-diastereomeric relationships. This case is *chirality-faithful*.
2. Stereoisograms of Type III involve two cases:
 - (a) *Chirality-faithful case*: As exemplified by Eq. 15, a pair of *C/A*-descriptors given to a pair of *RS*-diastereomers can be interpreted as being given to a pair of enantiomers.
 - (b) *Chirality-unfaithful case*: As exemplified by Eq. 22, a pair of *C/A*-descriptors given to a pair of *RS*-diastereomers cannot be interpreted as being given to a pair of enantiomers. A pair of lowercase letters *a/c* is used to characterize such a chirality-unfaithful case. Hence, Eq. 22 is revised as follows:

$$\left. \begin{array}{l} \mathbf{14} \quad OC-6-52-c \\ \mathbf{15} \quad OC-6-52-a \\ \overline{\mathbf{14}} \quad OC-6-62-c \\ \overline{\mathbf{15}} \quad OC-6-62-a \end{array} \right\} \quad (23)$$

3. A stereoisogram of Type V shows that a pair of *C/A*-descriptors given to a pair of *RS*-diastereomers are by no means applied to enantiomeric relationships. Each case of Type V is achiral so as to be characterized by the absence of enantiomers, while each case of Type III(b) is chiral so as to be characterized by the presence of enantiomers. In spite of this type of difference, the Type V case is also referred to as being *chirality-unfaithful*. A

pair of lowercase letters *a/c* is also used to characterize such a Type V case. Hence, Eq. 18 is revised as follows:

$$\left. \begin{array}{l} \mathbf{12} \quad OC-6-32-a \\ \mathbf{13} \quad OC-6-32-c \end{array} \right\} \quad (24)$$

Note again that chirality/achirality and *RS*-stereogenicity/*RS*-astereogenicity are independent concepts as summarized in Table 2, so that the capability of giving *C/A*-descriptors is assured by *RS*-stereogenicity (or *RS*-diastereomeric relationships), as summarized in Table 3.

Chirality-unfaithful cases (Type III(b) and Type V) correspond to cases characterized previously by the term “reflection-invariant descriptors” [43]. It is worthwhile here to point out the difference between their theoretical bases.

1. The examination of such chirality-unfaithful cases relies on the comparison concerning stereoisograms of Type III(b) and Type V. Examine, for example, the stereoisogram shown in Fig. 10 (Type V) as well as the stereoisogram shown in Fig. 12 (Type III(b)), where both (self-)enantiomeric and *RS*-diastereomeric relationships are taken into consideration as pairwise relationships.
2. On the other hand, the examination of such reflection-invariant cases relies on the comparison concerning (self-)enantiomeric relationships only, because diastereomeric relationships of the conventional stereochemistry are not pairwise relationships. Strictly speaking, moreover, such reflection-invariance does not necessarily hold true. For example, Fig. 12 (Type III(b)) shows that a reflection converts the sequence $a \rightarrow p \rightarrow q \rightarrow \bar{p}$ in **14** into another sequence $a \rightarrow p \rightarrow \bar{q} \rightarrow \bar{p}$ in **14**. These two sequences are different in q and \bar{q} so as to exhibit reflection-variance, even though assigned *C/A*-descriptors are reflection-invariant. On the other hand, Fig. 10 (Type V) shows that a reflection converts the sequence $a \rightarrow p \rightarrow \bar{p} \rightarrow a$ in **12** into the same sequence in **12** (= **12**) so as to exhibit reflection-invariance. Hence, the term “reflection-invariant” is concluded to be misleading.

The above discussions on chirality faithfulness reveal that the terms “asymmetric atoms”, “chirality units”, and “stereogenic units of type 1” (for Type I cases and Type III(a) cases) as well as terms “pseudoasymmetric atoms” and “stereogenic units of type 2” (for Type V cases and Type III(b) cases), which have been used in the conventional organic and inorganic stereochemistry [43, page 12], should be altogether replaced by the newly-defined term *RS-stereogenic atoms* or *units*, relying on stereoisograms of Types I, III, and V.

5 Conclusion

Stereoisograms of octahedral complexes are discussed in terms of attributive terms (chirality/achirality, *RS*-stereogenicity/*RS*-astereogenicity, and sclerality/asclerality) or equivalently in terms of relational terms (enantiomeric/self-enantiomeric, *RS*-diastereomeric/self-*RS*-diastereomeric, and holantimeric/self-holantimeric), where they are categorized into five types (Types I–V). The capability of giving *C/A*-descriptors is ascribed to *RS*-stereogenicity (or *RS*-diastereomeric relationships), so that stereoisograms of Type I, III, and V are characterized by *C/A*-descriptors because of their *RS*-stereogenicity. *RS*-Stereoisomeric groups controlling stereoisograms of octahedral complexes are examined as subgroups of a stereoisomeric group, so that

stereoisomerism of octahedral complexes are discussed comprehensively. The difference between *RS*-stereogenicity and stereogenicity as well as between *RS*-stereoisomerism and stereoisomerism is determined decisively after group-theoretical consideration. Thereby, the stereoisogram approach, which has originally been developed to rationalize organic stereochemistry [20, 26, 42], is clarified to be effective to inorganic stereochemistry.

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