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Stereoisograms of Octahedral Complexes. II. *RS*-Stereogenicity vs. Stereogenicity as Well as *RS*-Stereoisomerism vs. Stereoisomerism

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Abstract

Stereoisomeric groups are defined to describe the stereoisomerism of octahedral complexes by starting from *RS*-stereoisomeric groups for characterizing stereoisograms (cf. Part I of this series) and the symmetric group of degree 6. On the basis of the stereoisomeric groups, multiplets of stereoisograms are defined so as to clarify the difference between *RS*-stereoisomerism and stereoisomerism. Stereogenic groups are also defined as subgroups of the stereoisomeric groups, so that the difference between *RS*-stereogenicity and stereogenicity is determined decisively after group-theoretical consideration. Thus, stereogenicity is shown to have nothing to do with the capability of giving *C/A*-descriptors, which is, in turn, ascribed to *RS*-stereogenicity (or *RS*-diastereomeric relationships), but not to chirality. Both the concept of stereogenicity and the concept of *RS*-stereogenicity are concluded to be independent to the concept of chirality, although *RS*-stereogenicity interacts with chirality as formulated by a stereoisogram. Thereby, 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 clarified to be effective to inorganic stereochemistry.

1 Introduction

In Part I of this series, the stereoisogram approach developed originally for organic stereochemistry [1–3] has been applied to octahedral complexes, so that it has been shown to be effective to inorganic stereochemistry. Thus, stereoisograms of octahedral complexes have been discussed in terms of attributive terms (chirality, *RS*-stereogenicity, and sclerality) or equivalently in terms of relational terms (enantiomeric, *RS*-diastereomeric, and holantimeric). After they and categorized into five types (Types I–V), the conventional terminology has been thoroughly revised to assure consistency from a viewpoint of the stereoisogram approach.

This revision has influenced the conceptual basis of the conventional terminology and clarified its drawbacks overlooked for a long time. For example, the concept of a "stereogenic center" is defined in inorganic stereochemistry [4, page 58] as follows:

> **Quotation 1**
> "An atomic center in a molecule is called stereogenic if an interchange of two ligands leads to a stereoisomer. If the stereoisomer obtained is the other enantiomer of a pair, the atom is a chiral center."

This definition succeeds the counterpart of organic stereochemistry, as found in [5, page 53] and [6, pages 32–33]. Although these sentences seem to be valid, the "interchange of two ligands" in the first sentence does not conceptually contain a reflection operation, whereas the "interchange of two ligands" presumed in the word "enantiomer" of the second sentence contains a reflection operation. Note that, to examine whether they are enantiomeric, the enantiomer of the original molecule should be generated by reflection. The difference in connotations between the first "interchange of two ligands" ($\neq$ reflection) and the second "interchange of two ligands" ($=$ reflection) is unconsciously nullified in the total meaning of the definition, so that the "chiral center" and the "stereogenic center" in the definition have been recognized as if they stem from operations of the same kind. In other words, *RS*-diastereomeric relationships and enantiomeric relationships are mixed up in the conventional definition. As a result, the second sentence of Quotation 1 becomes misleading, although this misleading situation is difficult to be noticed because we used to pay our attention to Type I cases mainly and to Type V cases exceptionally. Examine Type III cases discussed in Part I of this series, on the other hand, where the stereoisomer obtained by an interchange of two ligands (i.e., the *RS*-diastereomer) in not identical with the enantiomer of a pair. Thereby, the definition described in Quotation 1 forces us to conclude that the central atom at issue is not a chiral center; this is obviously inconsistent.

This type of mixing-up about contributed operations causes latent confusions. Thus, the conventional definition results in an erroneous statement:

> **Quotation 2**
> "Stereogenic centers may, or may not be centers of chirality, but all chiral centers are stereogenic.",

as found in a textbook of inorganic stereochemistry [4, page 58] as well as in textbooks of organic stereochemistry [5, page 53] & [6, page 33]. In a similar way to the preceding paragraph, this statement unconsciously aims at Type I and V cases, so that the erroneous situation is difficult to be noticed. The erroneous situation in organic stereochemistry can be pointed out by the existence of Type II cases, which provide us with counterexamples of the 'but' phrase of the above Quotation 2. Hence, chirality has been concluded to be independent to stereogenicity (*RS*-stereogenicity), when we focus our attention on one central atom, where *RS*-stereogenicity

can be regarded as coinciding with stereogenicity for tetrahedral skeletons of organic stereochemistry [7].

On the other hand, the erroneous situation of the 'but' phrase in Quotation 2 exhibits more complicated features in inorganic stereochemistry, because *RS*-stereogenicity and stereogenicity do not always coincide with each other. In spite of such complicated features, chirality can be concluded to be independent to *RS*-stereogenicity and to stereogenicity even in inorganic stereochemistry. To reach this conclusion will be one of the tasks of the present article.

According to the stereoisogram approach described in Part I of this series, the conventional definition (Quotation 1) is replaced by a more specific one:

> A promolecule (or an atomic center in a promolecule) is called *RS-stereogenic* if an interchange of two ligands leads to the *RS*-diastereomer. A promolecule (or an atomic center in a promolecule) is called *chiral* if a reflection leads to the enantiomer of a pair. Chirality is conceptually independent to *RS*-stereogenicity, even if the *RS*-diastereomer is identical with the enantiomer of a pair.

Although the terms *RS-stereogenic* and *chiral* are originally concerned with the global symmetries of (pro)molecules, they can be used to characterize their atomic centers so long as such atomic centers exhibit the same local symmetries as the global ones (i.e., the fixed points under the global symmetries at issue). Thus, the term *RS-stereogenic centers* has been introduced by the stereoisogram approach, where the term *RS-stereogenic* is differentiated from the purely geometrical term *chiral*. Thereby, the statement quoted above (Quotation 2) is revised as follows:

> *RS*-Stereogenic centers may, or may not be centers of chirality (chiral: Type I, III; achiral: Type V). *RS*-Astereogenic (*RS*-non-stereogenic) centers may, or may not be centers of chirality (chiral: Type II; achiral: Type IV).

This revised statement connotes that *chiral centers are not always stereogenic*, because the term *stereogenic centers* contains the term *RS-stereogenic centers* conceptually, as discussed later in the present article. More precisely speaking, *RS*-stereogenicity and *RS*-astereogenicity as well as chirality and achirality should be discussed in terms of five types of stereoisograms (Type I–V).

According to the stereoisogram approach [1–3], a tetrahedral skeleton of organic stereochemistry is concluded to be a special case in which *RS*-stereogenicity coincides with stereogenicity, if we focus our attention on cases of one central atom. This special feature of the tetrahedral skeleton has once been pointed out in an alternative fashion [8]:

> **Quotation 3**
> "···, the regular tetrahedron is the only skeleton in which every transposition of ligands is equivalent to a reversal in the sense of chirality of the ligated assembly.",

although *RS*-diastereomeric relationships and enantiomeric relationships were mixed up on the same line as Quotation 1. In contrast to the tetrahedron skeleton, an octahedral skeleton of inorganic stereochemistry is a more general case in which *RS*-stereogenicity does not coincide with stereogenicity.

The separation of *RS*-stereogenicity from stereogenicity means that the remaining task is to examine the term "stereogenicity" in connection with the separate concept *RS-stereogenicity*. As an additional task, the term "stereoisomerism" as a more general term should be examined in connection with *RS*-stereoisomerism. In the present paper as Part II of this series, these tasks will be conducted by introducing a multiplet of stereoisograms as a new matter, where an octahedral skeleton is taken as a typical example.

2 Mathematical Formulations

2.1 Stereoisomeric Groups and Multiplets of Stereoisograms

2.1.1 *RS*-Stereoisomeric Groups

The construction of *RS*-stereoisomeric groups by starting from the point group $\mathbf{O}_h$ has been discussed in detail in Part I of this series. The cruxes are here summarized as reference to construct stereoisomeric groups.

The point group $\mathbf{O}_h$ acting on an octahedral skeleton is characterized by the coset decomposition $\mathbf{O}_h = \mathbf{O} + \mathbf{O}i$, where the representative i is an inversion. Let the symbol $\tilde{\imath}$ be an *RS*-permutation which converts the octahedral skeleton into an inverted skeleton with no ligand inversions. Let the symbol $\tilde{I}$ be a ligand inversion which causes ligand inversions without changing the skeleton, where $\tilde{\imath} = i\tilde{I}$. Then, the *RS*-stereoisomeric group $\mathbf{O}_{h\tilde{\imath}\tilde{I}}$ is defined by Eq. 1. Because the representative of each coset can be selected from any element contained in the coset, another set of representatives can be selected as shown in Eq. 2, where the symbol $\sigma_{h(1)}$ represents a reflection operation concerned with a mirror plane which contains four vertices of the octahedral skeleton and where $\tilde{\sigma}_{h(1)} = \sigma_{h(1)}\tilde{I}$.

$$\mathbf{O}_{h\tilde{\imath}\tilde{I}} = \mathbf{O} + \mathbf{O}i + \mathbf{O}\tilde{\imath} + \mathbf{O}\tilde{I} \tag{1}$$

$$= \mathbf{O} + \mathbf{O}\sigma_{h(1)} + \mathbf{O}\tilde{\sigma}_{h(1)} + \mathbf{O}\tilde{I}. \tag{2}$$

Because $\mathbf{O}$ is a normal subgroup of $\mathbf{O}_{h\tilde{\imath}\tilde{I}}$, the corresponding factor group is constructed as follows:

$$\mathbf{O}_{h\tilde{\imath}\tilde{I}}/\mathbf{O} = \{\mathbf{O}, \mathbf{O}i, \mathbf{O}\tilde{\imath}, \mathbf{O}\tilde{I}\} \tag{3}$$

$$= \{\mathbf{O}, \mathbf{O}\sigma_{h(1)}, \mathbf{O}\tilde{\sigma}_{h(1)}, \mathbf{O}\tilde{I}\}. \tag{4}$$

The factor group represented by Eq. 3 or equivalently by Eq. 4 is isomorphic to the Klein four-group. Obviously, the transversals of Eq. 1 and Eq. 2 give the following groups respectively:

$$\mathbf{O}_{h\tilde{\imath}\tilde{I}}/\mathbf{O} \sim \{I, i, \tilde{\imath}, \tilde{I}\} \tag{5}$$

$$\sim \{I, \sigma_{h(1)}, \tilde{\sigma}_{h(1)}, \tilde{I}\}, \tag{6}$$

both of which are isomorphic to the Klein four-group.

The six vertices of an octahedral skeleton constructs an equivalence class (orbit), which is governed by the coset representation of degree 6, i.e., $\mathbf{O}_h(/\mathbf{C}_{4v})$. The coset representation can be extended to a coset representation $\mathbf{O}_{h\tilde{\imath}\tilde{I}}(/\mathbf{C}_{4v\tilde{\sigma}\tilde{I}})$, where $\mathbf{C}_{4v\tilde{\sigma}\tilde{I}}$ is generated by starting from the group $\mathbf{C}_{4v}$ $(= \mathbf{C}_4 + \mathbf{C}_4\sigma_{h(2)})$ in a similar way to Eq. 2 (i.e., $\mathbf{O}$ is substituted for $\mathbf{C}_4$). The concrete form of the coset representation $\mathbf{O}_{h\tilde{\imath}\tilde{I}}(/\mathbf{C}_{4v\tilde{\sigma}\tilde{I}})$ has been shown in Fig. 2 of Part I of this series.

Suppose that the six vertices of an octahedral skeleton are numbered sequentially to give a reference skeleton **1** depicted in the upperleft of each stereoisogram of Fig. 1. The reference skeleton **1** corresponds to the identity element (I). The mode of numbering can be arbitrarily adopted without losing generality.

The transversal appearing in Eq. 5 corresponds to the following set of operations:

$$I \sim (1)(2)(3)(4)(5)(6) \tag{7}$$

$$i \sim \overline{(1\,6)(2\,4)(3\,5)} \tag{8}$$

$$\tilde{\imath} \sim (1\,6)(2\,4)(3\,5) \tag{9}$$

$$\tilde{I} \sim \overline{(1)(2)(3)(4)(5)(6)}, \tag{10}$$

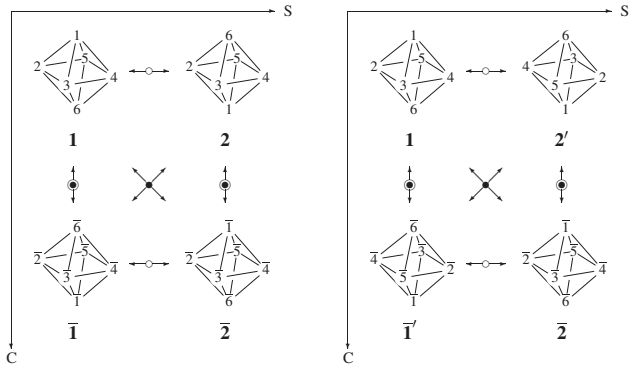


Figure 1: Reference stereoisograms for characterizing an octahedral skeleton, which are equivalent under the *RS*-stereoisomeric group.

where disjoint cycles without and with a bar are selected from $\mathbf{O}_{h\tilde{\imath}\tilde{I}}(/\mathbf{C}_{4v\tilde{\sigma}\tilde{I}})$. These operations construct a group isomorphic to the Klein four-group. This set of operations generates a reference stereoisogram in the right of Fig. 1.

On the same line, the transversal appearing in Eq. 6 corresponds the following set of operations:

$$I \sim (1)(2)(3)(4)(5)(6) \tag{11}$$
$$\sigma_{h(1)} \sim \overline{(1\,6)(2)(3)(4)(5)} \tag{12}$$
$$\tilde{\sigma}_{h(1)} \sim (1\,6)(2)(3)(4)(5) \tag{13}$$
$$\tilde{I} \sim \overline{(1)(2)(3)(4)(5)(6)}, \tag{14}$$

where disjoint cycles without and with a bar are selected from $\mathbf{O}_{h\tilde{\imath}\tilde{I}}(/\mathbf{C}_{4v\tilde{\sigma}\tilde{I}})$. These operations construct a group isomorphic to the Klein four-group. This set of operations generates a reference stereoisogram in the left of Fig. 1.

The two reference stereoisograms are equivalent under the *RS*-stereoisomeric group $\mathbf{O}_{h\tilde{\imath}\tilde{I}}$. Hence, we use the left stereoisogram as a reference.

2.1.2 Stereogenic Group for an Octahedral Skeleton

The *RS*-stereoisomeric group $\mathbf{O}_{h\tilde{\imath}\tilde{I}}$ (Eq. 1 or Eq. 2) contains the *RS*-permutation group (or *RS*-stereogenic group) as a subgroup, i.e.,

$$\mathbf{O}_{\tilde{\imath}} = \mathbf{O} + \mathbf{O}\tilde{\imath} = \mathbf{O} + \mathbf{O}\tilde{\sigma}_{h(1)}, \tag{15}$$

which is regarded as a permutation group of degree 6 ($|\mathbf{O}_{\tilde{\imath}}| = 48$). Because the *RS*-permutation group $\mathbf{O}_{\tilde{\imath}}$ is isomorphic to $\mathbf{O}_h$, it is tentatively equalized (as a group of permutations) to the coset representation $\mathbf{O}_h(/\mathbf{C}_{4v})$ without considering ligand reflections (cf. Fig. 2 of Part I of this series). By following this convention, the *RS*-permutation group $\mathbf{O}_{\tilde{\imath}}$ (Eq. 15) can be regarded as a subgroup of the symmetric group of degree 6 ($\mathbf{S}^{[6]}$), the order of which is calculated to

be $|\mathbf{S}^{[6]}| = 6! = 720$. Because the symmetric group of degree 6 ($\mathbf{S}^{[6]}$) generates stereoisomers with no ligand reflections, it is called *a stereogenic group* for octahedral complexes. A coset decomposition of the symmetric group $\mathbf{S}^{[6]}$ by the *RS*-permutation group $\mathbf{O}_{\bar{\imath}}$ is calculated as follows:

$$\begin{aligned}\mathbf{S}^{[6]} &= \mathbf{O}_{\bar{\imath}} + \mathbf{O}_{\bar{\imath}}(3\,4) + \mathbf{O}_{\bar{\imath}}(4\,5) \\ &\quad + \mathbf{O}_{\bar{\imath}}(2\,6) + \mathbf{O}_{\bar{\imath}}(2\,6)(3\,4) + \mathbf{O}_{\bar{\imath}}(2\,6)(4\,5) \\ &\quad + \mathbf{O}_{\bar{\imath}}(3\,6) + \mathbf{O}_{\bar{\imath}}(3\,4\,6) + \mathbf{O}_{\bar{\imath}}(3\,6)(4\,5) \\ &\quad + \mathbf{O}_{\bar{\imath}}(4\,6) + \mathbf{O}_{\bar{\imath}}(3\,6\,4) + \mathbf{O}_{\bar{\imath}}(4\,6\,5) \\ &\quad + \mathbf{O}_{\bar{\imath}}(5\,6) + \mathbf{O}_{\bar{\imath}}(3\,4)(5\,6) + \mathbf{O}_{\bar{\imath}}(4\,5\,6), \end{aligned} \tag{16}$$

where a 1-cycle is omitted so that a shortened disjoint cycle $(3\,4)$, for example, represents a disjoint cycle $(1)(2)(3\,4)(5)(6)$ as a full list of cycles. The number of the cosets are calculated to be $|\mathbf{S}^{[6]}|/|\mathbf{O}_{\bar{\imath}}| = 720/48 = 15$.

The normalizer $N(\mathbf{O}_{\bar{\imath}})$ of the *RS*-permutation group $\mathbf{O}_{\bar{\imath}}$ in the symmetric group $\mathbf{S}^{[6]}$ is found to be the *RS*-permutation group $\mathbf{O}_{\bar{\imath}}$ itself (this has been confirmed by using the Maple system), so that the number of conjugate subgroups of $\mathbf{O}_{\bar{\imath}}$ is calculated to be $|\mathbf{S}^{[6]}|/|N(\mathbf{O}_{\bar{\imath}})| = |\mathbf{S}^{[6]}|/|\mathbf{O}_{\bar{\imath}}| = 720/48 = 15$. Hence, the 15 cosets appearing in the right-hand side of Eq. 16 generate respective conjugate subgroups of $\mathbf{O}_{\bar{\imath}}$, which fix the corresponding cosets, e.g., the subgroup $(3\,4)^{-1}\mathbf{O}_{\bar{\imath}}(3\,4)$ fixes the coset $\mathbf{O}_{\bar{\imath}}(3\,4)$.

2.1.3 Stereoisomeric Group for an Octahedral Skeleton

The representatives of the cosets appearing in the right-hand side of Eq. 16 are operated onto the *RS*-stereoisomeric group $\mathbf{O}_{h\bar{\imath}I}$ (Eq. 1 or Eq. 2) so as to give a further group:

$$\begin{aligned}\mathbf{S}^{[6]}_{\mathbf{O}_{h\bar{\imath}I}} &= \mathbf{O}_{h\bar{\imath}I} + \mathbf{O}_{h\bar{\imath}I}(3\,4) + \mathbf{O}_{h\bar{\imath}I}(4\,5) \\ &\quad + \mathbf{O}_{h\bar{\imath}I}(2\,6) + \mathbf{O}_{h\bar{\imath}I}(2\,6)(3\,4) + \mathbf{O}_{h\bar{\imath}I}(2\,6)(4\,5) \\ &\quad + \mathbf{O}_{h\bar{\imath}I}(3\,6) + \mathbf{O}_{h\bar{\imath}I}(3\,4\,6) + \mathbf{O}_{h\bar{\imath}I}(3\,6)(4\,5) \\ &\quad + \mathbf{O}_{h\bar{\imath}I}(4\,6) + \mathbf{O}_{h\bar{\imath}I}(3\,6\,4) + \mathbf{O}_{h\bar{\imath}I}(4\,6\,5) \\ &\quad + \mathbf{O}_{h\bar{\imath}I}(5\,6) + \mathbf{O}_{h\bar{\imath}I}(3\,4)(5\,6) + \mathbf{O}_{h\bar{\imath}I}(4\,5\,6), \end{aligned} \tag{17}$$

which is called *the stereoisomeric group* of an octahedral skeleton. The order of the stereoisomeric group $\mathbf{S}^{[6]}_{\mathbf{O}_{h\bar{\imath}I}}$ is calculated to be $|\mathbf{S}^{[6]}_{\mathbf{O}_{h\bar{\imath}I}}| = |\mathbf{O}_{h\bar{\imath}I}| \times 15 = 96 \times 15 = 1440$.

The stereoisomeric group $\mathbf{S}^{[6]}_{\mathbf{O}_{h\bar{\imath}I}}$ is also constructed by a direct product $\mathbf{S}^{[6]} \times \{I, i\}$, which is isomorphic to $\mathbf{S}^{[6]} \times \mathbf{S}^{[2]}$. On the same line, the *RS*-stereoisomeric group $\mathbf{O}_{h\bar{\imath}I}$ is also constructed by a direct product $\mathbf{O}_{\bar{\imath}} \times \{I, i\}$. This mode of construction is conducted by a program of the Maple language so as to reveal that the normalizer $N(\mathbf{O}_{h\bar{\imath}I})$ of the *RS*-stereoisomeric group $\mathbf{O}_{h\bar{\imath}I}$ in the stereoisomeric group $\mathbf{S}^{[6]}_{\mathbf{O}_{h\bar{\imath}I}}$ is the $\mathbf{O}_{h\bar{\imath}I}$ group itself. Hence, the number of conjugate subgroups of the $\mathbf{O}_{h\bar{\imath}I}$ group is calculated to be

$$\frac{|\mathbf{S}^{[6]}_{\mathbf{O}_{h\bar{\imath}I}}|}{|N(\mathbf{O}_{h\bar{\imath}I})|} = \frac{|\mathbf{S}^{[6]}_{\mathbf{O}_{h\bar{\imath}I}}|}{|\mathbf{O}_{h\bar{\imath}I}|} = \frac{1440}{96} = 15. \tag{18}$$

As a result, the 15 cosets appearing in the right-hand side of Eq. 17 generate respective conjugate subgroups of $\mathbf{O}_{h\bar{\imath}I}$, which fix the corresponding cosets, e.g., the subgroup $(3\,4)^{-1}\mathbf{O}_{h\bar{\imath}I}(3\,4)$ fixes the coset $\mathbf{O}_{h\bar{\imath}I}(3\,4)$.

2.1.4 Multiplets of Stereoisograms for an Octahedral Skeleton

The respective cosets appearing in the stereoisomeric group $\mathbf{S}^{[6]}_{\mathbf{O}_{h\bar{1}\bar{1}}}$ (Eq. 17) generate a set of 15 reference stereoisograms, each of which is stereoisomeric to the original reference stereoisogram shown in Fig. 1. The set (multiplet) of the 15 reference stereoisograms is shown in Fig. 2, where the stereoisogram **9** is identical with the reference stereoisogram shown in the left of Fig. 1, i.e., $\mathbf{1} = \mathbf{3}$, $\mathbf{2} = \mathbf{4}$, $\overline{\mathbf{1}} = \overline{\mathbf{3}}$, and $\overline{\mathbf{2}} = \overline{\mathbf{4}}$.

The 15 reference stereoisograms (**9**, **10**, **11**, etc.) shown in Fig. 2 indicate respective modes of numbering, each of which belongs to one of the conjugate subgroups described above. For example, the reference stereoisogram **10** belongs to the subgroup $(3\ 4)^{-1}\mathbf{O}_{h\bar{1}\bar{1}}(3\ 4)$ corresponding to the coset $\mathbf{O}_{h\bar{1}\bar{1}}(3\ 4)$. The 15 reference stereoisograms collected in Fig. 2 generate a maximum of 15 quadruplets of *RS*-stereoisomers, when an appropriate set of ligands is placed on their vertices.

The three reference stereoisograms in each of the five rows in Fig. 2 have a common vertical pair of vertices, e.g., 1 and 6 for the first row, 1 and 2 for the second row, etc., where the number 1 vertex is always placed at the top of each octahedron without losing generality. Each column of Fig. 2 corresponds to a permutation within a horizontal plain perpendicular to the common vertical pair of vertices.

2.2 Terminology

In the conventional stereochemistry, the terms "stereogenicity" and "stereoisomerism" are not so well differentiated, as found in Quotation 1 of the Introduction. Before we examine octahedral complexes, we will briefly discuss the terminology used in the stereoisogram approach.

2.2.1 The Terms *Stereogenicity* and *Diastereomeric*

From one viewpoint on equivalence classes (orbits), the relationship between any two of the 15 reference stereoisograms (i.e., **9**, **10**, **11**, etc.) are referred to as being *ortho-diastereomeric* if we take account of the stereogenic group $\mathbf{S}^{[6]}$ (Eq. 16). To treat cases of stereogenic groups other than $\mathbf{S}^{[6]}$, this specific case is generalized as follows:

Definition 1 (Ortho-stereogenic and Ortho-diastereomeric)
The relational term *ortho-diastereomeric* is used to refer to a relationship *between inequivalent stereoisograms* of the same constitution under the action of a stereogenic group (e.g., $\mathbf{S}^{[6]}$ of Eq. 16). The attributive term *ortho-stereogenic* is used if there appears such an ortho-diastereomeric relationship between a stereoisogram and any other stereoisogram.

Although the original specification of Def. 1 is concerned with stereoisograms, a promolecule contained in a stereoisogram can be regarded as being ortho-diastereomeric to a promolecule contained in another stereoisogram, if these two promolecules are convertible under $\mathbf{S}^{[6]}$ (Eq. 16). Moreover, a pair of enantiomeric promolecules contained in a stereoisogram can be regarded as being ortho-diastereomeric to a pair of enantiomeric promolecules contained in another stereoisogram, if these two pairs are convertible under $\mathbf{S}^{[6]}$ (Eq. 16).

Definition 2 (*RS*-stereogenic and *RS*-diastereomeric)
The relational term *RS-diastereomeric* is used to refer to inequivalency within a stereoisogram under the action of an *RS*-permutation group (e.g., $\mathbf{O}_{\bar{i}}$ of Eq. 15). The attributive term

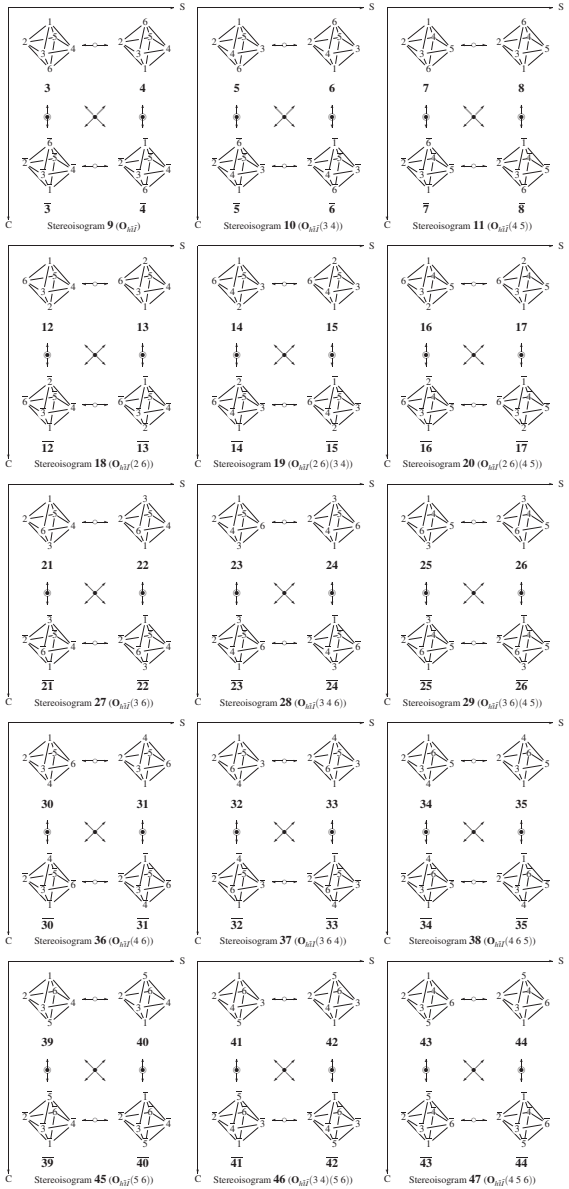


Figure 2: Multiplet of 15 reference stereoisograms for giving octahedral complexes

RS-stereogenic is used if there appears such an *RS*-diastereomeric relationship in the stereoisogram.

Note that the term *RS-diastereomeric* can be regarded as being concerned with the relationship *between pairs of enantiomers* within a stereoisogram, as discussed in detail in the following paragraphs.

According to Def. 2, a promolecule contained in a stereoisogram is regarded as being *RS*-diastereomeric to a promolecule contained in the same stereoisogram, if these two promolecules are convertible under the *RS*-permutation group $\mathbf{O}_{\tilde{\imath}}$, which is a subgroup of the stereogenic group $\mathbf{S}^{[6]}$. Moreover, a pair of enantiomeric promolecules contained in a stereoisogram can be regarded as being *RS*-diastereomeric to a pair of enantiomeric promolecules contained in the same stereoisogram, if these two pairs are convertible under $\mathbf{O}_{\tilde{\imath}}$.

The action of the stereogenic group $\mathbf{S}^{[6]}$ means no interconversions between a skeleton and its mirror image. That is to say, a pair of *RS*-diastereomers, **3** (=**1**) and **4** (=**2**), constructs an orbit of equivalent skeletons under the action of the stereogenic group $\mathbf{S}^{[6]}$, while another pair of *RS*-diastereomers, $\overline{\mathbf{3}}$ (= $\overline{\mathbf{1}}$) and $\overline{\mathbf{4}}$ (= $\overline{\mathbf{2}}$), constructs another orbit of equivalent skeletons under the action of the $\mathbf{S}^{[6]}$. It is inconvenient to do such dual reference to the respective cases.

To avoid the inconvenience, we adopt a convention that each pair of enantiomers is treated as a unit. Thereby, enantiomeric pairs of promolecules and achiral promolecules (self-enantiomeric pairs) can be treated in an integrated fashion. Thus, a pair of **3**/$\overline{\mathbf{3}}$ and another pair of **4**/$\overline{\mathbf{4}}$ are regarded as being *RS*-diastereomeric, i.e., interconvertible under the *RS*-permutation group $\mathbf{O}_{\tilde{\imath}}$, which is a subgroup of the stereogenic group $\mathbf{S}^{[6]}$. In addition, the pair of **3**/$\overline{\mathbf{3}}$ and a further pair of **5**/$\overline{\mathbf{5}}$ are regarded as being ortho-diastereomeric, i.e., interconvertible under the stereogenic group $\mathbf{S}^{[6]}$.

This convention provides us with a new definition of *stereogenicity*, which can be used in place of the conventional concept of "stereogenicity".

Definition 3 (Stereogenic and Diastereomeric)

The relational term *diastereomeric* is used to refer to a relationship *between inequivalent pairs of enantiomers* (or achiral promolecules) with the same constitution under the action of the stereogenic group (e.g., $\mathbf{S}^{[6]}$ of Eq. 16). The attributive term *stereogenic* is used if there appears such an ortho-diastereomeric relationship between a pair of enantiomers and any other pair of enantiomers.

This definition aims at harmony with the conventional term "diastereomeric" (the attributive term "stereogenic" of Quotation 1). However, the stereogenicity of Def. 3 is conceptually different from the "stereogenicity" of Quotation 1, because the former (Def. 3) does not refer to chirality while the latter (Quotation 1) refers to chirality by mixing up diastereomeric (Def. 3, or more precisely speaking, *RS*-diastereomeric) relationships and enantiomeric ones.

By comparing Def. 2 with Def. 3, the concept of *RS*-stereogenicity of Def. 2 is concluded to be contained in the concept of stereogenicity of Def. 3, i.e.,

$$RS\text{-stereogenicity} \subset \text{stereogenicity}, \tag{19}$$

because an *RS*-permutation (as a rotation) for Def. 2 is contained in $\mathbf{S}^{[6]}$ for Def. 3, i.e., $\mathbf{O}_{\tilde{\imath}} \subset \mathbf{S}^{[6]}$ (cf. Eq. 16). Note that the *RS*-stereogenicity (as well as the stereogenicity) is an independent

concept to the concept of chirality, as specified by stereoisograms. This means that diastereomeric relationships of Def. 3 are independently determined apart from enantiomeric relationships, which have, in turn, been determined concordantly with *RS*-diastereomeric relationships (Def. 2) by means of stereoisograms, prior to the application of Def. 3.

As discussed in the preceding paragraph, the application of Def. 2 should precede the application of Def. 3 in order to avoid confusions. This precedence of Def. 2 over Def. 3 means that the term *diastereomeric* (or *stereogenic*) of Def. 3 is used in the meaning of the term *ortho-diastereomeric* (or *ortho-stereogenic*) of Def. 1. To prevent confusions, however, the following expressions should be used:

1. The expression "*RS*-stereogenic and stereogenic" is permitted to refer to "*RS*-stereogenic and ortho-stereogenic" cases.

2. The expression "*RS*-stereogenic" is permitted to refer to "*RS*-stereogenic and not ortho-stereogenic" cases.

3. The expression "not *RS*-stereogenic and stereogenic" is permitted to refer to "not *RS*-stereogenic and ortho-stereogenic" cases.

2.2.2 The Terms *Stereoisomerism* and *Stereoisomeric*

From the other viewpoint on equivalence classes (orbits), the relationship between any two of the 15 reference stereoisograms is referred to as being *stereoisomeric* if we take account of inequivalent stereoisograms under the stereoisomeric group $\mathbf{S}^{[6]}_{\mathbf{O}_{hi\bar{I}}}$ (Eq. 17). Because the octahedral skeleton is capable of generating stereoisomeric stereoisograms, the capability is referred to as being stereoisomerous [9]. The phenomena of being stereoisomerous is referred to by the term *stereoisomerism*. The relationship between any two of the four components of a stereoisogram is referred to as being *RS*-stereoisomeric, where it is more detailedly referred to as being *RS*-diastereomeric, enantiomeric, or holantimeric. Because the octahedral skeleton is capable of generating a quadruplet of *RS*-stereoisomers (i.e., a stereoisogram), the capability is referred to as being *RS*-stereoisomerous, where it is more detailedly referred to as being *RS*-stereogenic, chiral, or scleral. The phenomena of being *RS*-stereoisomerous is referred to by the term *RS-stereoisomerism*. Note that the relational term *stereoisomeric* (the attributive term: stereoisomerous [9]) is concerned with inequivalent stereoisograms under the action of the stereoisomeric group $\mathbf{S}^{[6]}_{\mathbf{O}_{hi\bar{I}}}$ (Eq. 17), while the relational term *RS-stereoisomeric* (the attributive term: *RS*-stereoisomerous) is concerned with inequivalent stereoisograms under the action of the *RS*-stereoisomeric group $\mathbf{O}_{hi\bar{I}}$ (Eq. 1 or Eq. 2).

3 Stereoisomers of Octahedral Complexes

3.1 Stereoisomers of Octahedral Complexes with Achiral Proligands

Derivation of octahedral complexes is formulated to be substitution of a set of proligands on the vertices of reference stereoisograms shown in Fig. 2, where the mode of substitution is specified in terms of a function which determines a proligand to be placed on each vertex. When we take account of achiral proligands only, the resulting stereoisograms belong to Type I or IV. Stereoisograms of other types (Type II, III, and V) do not appear.

3.1.1 Octahedral Complexes with Six Different Achiral Proligands ([Mabcdef])

Suppose that six achiral proligands of different kinds (a, b, c, d, e, and f) are placed on the six vertices of the reference octahedron skeleton **1** (the same as **3** in Fig. 2), where the substitution mode is represented by the following function:

$$f_1: \quad f_1(1)=\mathrm{a}, f_1(2)=\mathrm{b}, f_1(3)=\mathrm{c}, f_1(4)=\mathrm{d}, f_1(5)=\mathrm{e}, f_1(6)=\mathrm{f}. \tag{20}$$

This substitution mode may be selected otherwise without losing generality, so long as the constitution is not changed. The function f_1 is applied to the 15 reference stereoisograms shown in Fig. 2, where the central metal (M) is omitted and where we place $\overline{\mathrm{a}}=\mathrm{a}$, $\overline{\mathrm{b}}=\mathrm{b}$, $\overline{\mathrm{c}}=\mathrm{c}$, $\overline{\mathrm{d}}=\mathrm{d}$, $\overline{\mathrm{e}}=\mathrm{e}$, and $\overline{\mathrm{f}}=\mathrm{f}$, because these proligands are achiral in isolation (when detached). In the present article, a letter with an overbar represents a mirror image of its original letter, whether the letters denote proligands or promolecules.

The resulting 15 stereoisograms of Type I (Fig. 3) correspond to 15 quadruplets of *RS*-stereoisomers, each of which is degenerated to a pair of enantiomers. The number 15 is consistent to the previous result of combinatorial enumeration [10], where each enantiomeric pair is counted once and belongs to the point group $\mathbf{C}_1$, as reported in the partition-[111111]-row of Table 5 of [10].

According to the IR-9.3.3.4 and IR-9.3.4.8 of the IUPAC recommendations 2005 [11], a configuration index combined with an *C/A*-descriptor is assigned to a pair of *RS*-diastereomers (not to a pair of enantiomers) which is contained in each of the 15 stereoisograms collected in Fig. 3, where the CIP priority is presumed to be a > b > c > d > e > f.

48 *OC-6-64-A*
49$(=\overline{\mathbf{48}})$ *OC-6-64-C*
$(\mathbf{C}_1)$ Stereoisogram **54** $(\mathbf{O}_{h\tilde{i}\tilde{I}})$ (Type I) (21)

50 *OC-6-63-A*
51$(=\overline{\mathbf{50}})$ *OC-6-63-C*
$(\mathbf{C}_1)$ Stereoisogram **55** $(\mathbf{O}_{h\tilde{i}\tilde{I}}(3\,4))$ (Type I) (22)

52 *OC-6-65-A*
53$(=\overline{\mathbf{52}})$ *OC-6-65-C*
$(\mathbf{C}_1)$ Stereoisogram **56** $(\mathbf{O}_{h\tilde{i}\tilde{I}}(4\,5))$ (Type I) (23)

57 *OC-6-25-A*
58$(=\overline{\mathbf{57}})$ *OC-6-25-C*
$(\mathbf{C}_1)$ Stereoisogram **63** $(\mathbf{O}_{h\tilde{i}\tilde{I}}(2\,6))$ (Type I) (24)

59 *OC-6-26-C*
60$(=\overline{\mathbf{59}})$ *OC-6-26-A*
$(\mathbf{C}_1)$ Stereoisogram **64** $(\mathbf{O}_{h\tilde{i}\tilde{I}}(2\,6)(3\,4))$ (Type I) (25)

61 *OC-6-24-A*
62$(=\overline{\mathbf{61}})$ *OC-6-24-C*
$(\mathbf{C}_1)$ Stereoisogram **65** $(\mathbf{O}_{h\tilde{i}\tilde{I}}(2\,6)(4\,5))$ (Type I) (26)

66 *OC-6-34-C*
67$(=\overline{\mathbf{66}})$ *OC-6-34-A*
$(\mathbf{C}_1)$ Stereoisogram **72** $(\mathbf{O}_{h\tilde{i}\tilde{I}}(3\,6))$ (Type I) (27)

68 *OC-6-36-A*
69$(=\overline{\mathbf{68}})$ *OC-6-36-C*
$(\mathbf{C}_1)$ Stereoisogram **73** $(\mathbf{O}_{h\tilde{i}\tilde{I}}(3\,4\,6))$ (Type I) (28)

70 *OC-6-35-C*
71$(=\overline{\mathbf{70}})$ *OC-6-35-A*
$(\mathbf{C}_1)$ Stereoisogram **74** $(\mathbf{O}_{h\tilde{i}\tilde{I}}(3\,6)(4\,5))$ (Type I) (29)

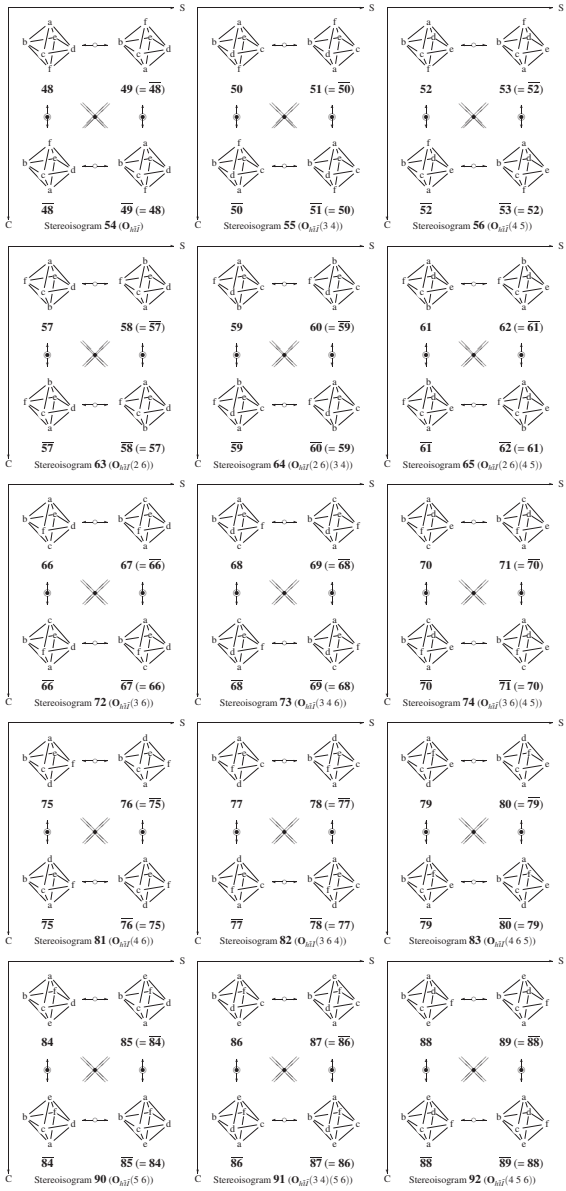


Figure 3: Multiplet of stereoisograms for representing 15 stereoisomers (enantiomeric pairs) of octahedral complexes with [Mabcdef]. The CIP priority: a > b > c > d > e > f.

$$\left.\begin{array}{ll} \mathbf{75} & \textit{OC-6-46-A} \\ \mathbf{76}(=\overline{\mathbf{75}}) & \textit{OC-6-46-C} \end{array}\right\} \quad (\mathbf{C}_1) \quad \text{Stereoisogram } \mathbf{81}\ (\mathbf{O}_{h\tilde{\imath}\tilde{I}}(4\ 6))\ \text{(Type I)} \tag{30}$$

$$\left.\begin{array}{ll} \mathbf{77} & \textit{OC-6-43-C} \\ \mathbf{78}(=\overline{\mathbf{77}}) & \textit{OC-6-43-A} \end{array}\right\} \quad (\mathbf{C}_1) \quad \text{Stereoisogram } \mathbf{82}\ (\mathbf{O}_{h\tilde{\imath}\tilde{I}}(3\ 6\ 4))\ \text{(Type I)} \tag{31}$$

$$\left.\begin{array}{ll} \mathbf{79} & \textit{OC-6-45-A} \\ \mathbf{80}(=\overline{\mathbf{79}}) & \textit{OC-6-45-C} \end{array}\right\} \quad (\mathbf{C}_1) \quad \text{Stereoisogram } \mathbf{83}\ (\mathbf{O}_{h\tilde{\imath}\tilde{I}}(4\ 6\ 5))\ \text{(Type I)} \tag{32}$$

$$\left.\begin{array}{ll} \mathbf{84} & \textit{OC-6-54-A} \\ \mathbf{85}(=\overline{\mathbf{84}}) & \textit{OC-6-54-C} \end{array}\right\} \quad (\mathbf{C}_1) \quad \text{Stereoisogram } \mathbf{90}\ (\mathbf{O}_{h\tilde{\imath}\tilde{I}}(5\ 6))\ \text{(Type I)} \tag{33}$$

$$\left.\begin{array}{ll} \mathbf{86} & \textit{OC-6-53-A} \\ \mathbf{87}(=\overline{\mathbf{86}}) & \textit{OC-6-53-C} \end{array}\right\} \quad (\mathbf{C}_1) \quad \text{Stereoisogram } \mathbf{91}\ (\mathbf{O}_{h\tilde{\imath}\tilde{I}}(3\ 4)(5\ 6))\ \text{(Type I)} \tag{34}$$

$$\left.\begin{array}{ll} \mathbf{88} & \textit{OC-6-56-A} \\ \mathbf{89}(=\overline{\mathbf{88}}) & \textit{OC-6-56-C} \end{array}\right\} \quad (\mathbf{C}_1) \quad \text{Stereoisogram } \mathbf{92}\ (\mathbf{O}_{h\tilde{\imath}\tilde{I}}(4\ 5\ 6))\ \text{(Type I)} \tag{35}$$

The CIP priority of temporary mirror-image proligands $\overline{\mathrm{a}} > \overline{\mathrm{b}} > \overline{\mathrm{c}} > \overline{\mathrm{d}} > \overline{\mathrm{e}} > \overline{\mathrm{f}}$ is obtained to be equal to the CIP priority of the original ligands, i.e., $\mathrm{a} > \mathrm{b} > \mathrm{c} > \mathrm{d} > \mathrm{e} > \mathrm{f}$. This means that all the cases of Fig. 3 are chirality-faithful [12]. Hence, the *C/A*-descriptor assigned to each pair of *RS*-diastereomers (Eqs. 21–35) can be regarded as being assigned to a pair of enantiomers. This discussion on chirality faithfulness is necessary to assure consistency to cases of Type III and V, although it appears to be artificial in Type I cases.

Each promolecule (an octahedral complex) in a stereoisogram shown in Fig. 3 is *RS*-stereogenic under the action of the *RS*-permutation group (or the *RS*-stereogenic group, i.e., $\mathbf{O}_{\tilde{\imath}}$), because the relevant stereoisogram of Type I is characterized to be *RS*-stereogenic. For example, **48** has its *RS*-diastereomer (**49**) which is identical with its enantiomer ($\overline{\mathbf{48}}$). Thus, such *RS*-stereogenicity as originally characterizing a stereoisogram is used to characterize promolecules contained in the stereoisogram.

According to the convention based on Def. 2, an enantiomeric pair of **48**/$\overline{\mathbf{48}}$ is tentatively differentiated from an enantiomeric pair of **49**/$\overline{\mathbf{49}}$ (even though it is afterward equalized to a pair of $\overline{\mathbf{48}}$/**48**) so as to be in an *RS*-diastereomeric relationship during the process of examining the relevant stereoisogram. In terms of Def. 3, the relationship between the pair of enantiomers **48**/$\overline{\mathbf{48}}$ and the pair of enantiomers **49**/$\overline{\mathbf{49}}$ (= $\overline{\mathbf{48}}$/**48**) is diastereomeric (also *RS*-diastereomeric) in the same stereoisogram. On the other hand, the relationship between the pair of enantiomers **48**/$\overline{\mathbf{48}}$ and a pair of enantiomers **50**/$\overline{\mathbf{50}}$ is diastereomeric (not *RS*-diastereomeric) in the different stereoisograms. This convention is artificial to these cases of Type I, but necessary to charcterize Type III and V cases.

Each quadruplet of *RS*-stereoisomers (each stereoisogram) shown in Fig. 3 is *RS*-stereogenic and stereogenic. This statement is allowable, though it is slightly vague because of Eq. 19. More decisively speaking, they are *RS*-stereogenic and ortho-stereogenic. Thus, the term *ortho-stereogenic* of Def. 1 is useful for the purpose of a more specific characterization of stereogenicity which do not coincide with *RS*-stereogenicity. It follows that all of the quadruplets of *RS*-stereoisomers (all of the stereoisograms) shown in Fig. 3 are concluded to be *RS*-stereogenic under the *RS*-permutation group $\mathbf{O}_{\tilde{\imath}}$ (Eq. 15) as well as to be ortho-stereogenic under the action of the stereogenic group $\mathbf{S}^{[6]}$ (Eq. 16).

3.1.2 Octahedral Complexes with [Ma_2bcde]

Six achiral proligands (2a, b, c, d, and e) are placed on the six vertices of the reference octahedron skeleton **1** (the same as **3** in Fig. 2), where the substitution mode is represented by the following function:

$$f_2: \quad f_2(1)=\mathrm{a}, f_2(2)=\mathrm{b}, f_2(3)=\mathrm{c}, f_2(4)=\mathrm{d}, f_2(5)=\mathrm{e}, f_2(6)=\mathrm{a}. \tag{36}$$

This function is applied to the 15 reference stereoisograms shown in Fig. 2. The resulting 15 stereoisograms (Fig. 4) exhibit several sets of coincidence in accord with the previous result of combinatorial enumeration [10], which shows the presence of three achiral promolecules of $\mathbf{C}_s$ and six enantiomeric pairs of $\mathbf{C}_1$ (the partition-[21111]-row of Table 5 in [10]).

The three achiral promolecules of $\mathbf{C}_s$ correspond to the stereoisograms of Type IV shown in the top row of Fig. 4, i.e., **96**, **97**, and **98**. In each of these stereoisograms of Type IV, a quadruplet of *RS*-stereoisomers is degenerated into a single achiral promolecule, i.e., **93**, **94**, or **95**, which is characterized by the following configuration index according to the IR-9.3.3.4 of the IUPAC recommendations 2005 [11]:

93 *OC-6-14* ($\mathbf{C}_s$) Stereoisogram **96** ($\mathbf{O}_{h\bar{1}\bar{1}}$) (Type IV) (37)

94 *OC-6-13* ($\mathbf{C}_s$) Stereoisogram **97** ($\mathbf{O}_{h\bar{1}\bar{1}}(3\,4)$) (Type IV) (38)

95 *OC-6-15* ($\mathbf{C}_s$) Stereoisogram **98** ($\mathbf{O}_{h\bar{1}\bar{1}}(3\,4)(4\,5)$) (Type IV) (39)

Although the presence of three achiral promolecules of $\mathbf{C}_s$ was shown correctly in the partition-[21111]-row of Table 5 in [10], the structures of **36**, **37**, and **38** in Fig. 2 of [10] were typeset incorrectly. They should be corrected as the structures **93**, **94**, and **95**, respectively.

Each $\mathbf{C}_s$-promolecule (**93**, **94**, or **95**) is *RS*-astereogenic (or *RS*-non-stereogenic) under the action of the *RS*-permutation group (or the *RS*-stereogenic group, i.e., $\mathbf{O}_I$) in accord with its stereoisogram of Type IV. On the other hand, each quadruplet of *RS*-stereoisomers (each stereoisogram, **96**, **97**, or **98**) is referred to as being ortho-stereogenic under the action of the stereogenic group $\mathbf{S}^{[6]}$ (Eq. 16). Hence, the $\mathbf{C}_s$-promolecules (**93**, **94**, and **95**) are referred to as being ortho-stereogenic according to Def. 1, although they are *RS*-astereogenic (or *RS*-non-stereogenic). This feature is permissible to be characterized by saying that the $\mathbf{C}_s$-promolecules (**93**, **94**, and **95**) are not *RS*-stereogenic but stereogenic.

Each of the six enantiomeric pairs of chiral $\mathbf{C}_1$-promolecules corresponds to a set of two stereoisograms of Type I, which are equivalent under the action of a subgroup of the stereoisomeric group. Note that the subgroup corresponds to [Ma_2bcde] produced by the subduction of a full symmetric [Ma_6]. For example, a quadruplet of **99/100** (= $\overline{\mathbf{99}}$) in the stereoisogram **105** is equivalent to a quadruplet of **117/118** (= $\overline{\mathbf{117}}$) in the stereoisogram **123**. Each quadruplet of *RS*-stereoisomers listed in the second and lower rows of Fig. 4 is degenerated into a pair of enantiomers. According to the IR-9.3.3.4 and IR-9.3.4.8 of the IUPAC recommendations 2005 [11], a configuration index combined with a *C/A*-descriptor is assigned to a pair of *RS*-diastereomers (not to a pair of enantiomers), where the CIP priority is presumed to be a > b > c > d > e.

99 *OC-6-42-C*
100(= $\overline{\mathbf{99}}$) *OC-6-42-A*
} ($\mathbf{C}_1$) Stereoisogram **105** ($\mathbf{O}_{h\bar{1}\bar{1}}(2\,6)$) (Type I) (40)

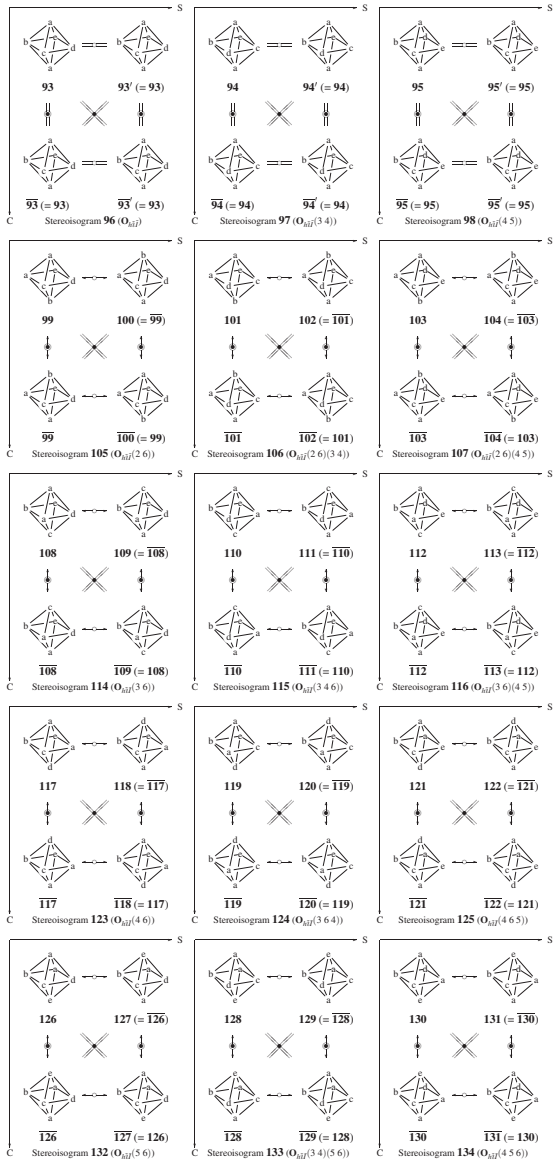


Figure 4: Multiplet of stereoisograms for representing stereoisomers (6 enantiomeric pairs and 3 achiral compounds) of octahedral complexes with [Ma_2bcde]. The CIP priority: a > b > c > d > e.

(equivalent to Stereoisogram **123**)

101 *OC-6-32-C*
102(= **101**) *OC-6-32-A* } ($\mathbf{C}_1$) Stereoisogram **106** ($\mathbf{O}_{h\bar{1}\bar{1}}$(2 6)(3 4)) (Type I) (41)

(equivalent to Stereoisogram **115**)

103 *OC-6-52-C*
104(= **103**) *OC-6-52-A* } ($\mathbf{C}_1$) Stereoisogram **107** ($\mathbf{O}_{h\bar{1}\bar{1}}$(2 6)(4 5)) (Type I) (42)

(equivalent to Stereoisogram **134**)

108 *OC-6-53-A*
109(= **108**) *OC-6-53-C* } ($\mathbf{C}_1$) Stereoisogram **114** ($\mathbf{O}_{h\bar{1}\bar{1}}$(3 6)) (Type I) (43)

(equivalent to Stereoisogram **132**)

112 *OC-6-43-A*
113(= **112**) *OC-6-43-C* } ($\mathbf{C}_1$) Stereoisogram **116** ($\mathbf{O}_{h\bar{1}\bar{1}}$(3 6)(4 5)) (Type I) (44)

(equivalent to Stereoisogram **125**)

119 *OC-6-54-A*
120(= **119**) *OC-6-54-C* } ($\mathbf{C}_1$) Stereoisogram **124** ($\mathbf{O}_{h\bar{1}\bar{1}}$(3 6 4)) (Type I) (45)

(equivalent to Stereoisogram **133**)

As for $\mathbf{C}_1$-promolecules of Type I (**99** etc.) in Fig. 4, *RS*-stereogenicity (and *RS*-diastereomeric relationships) as well as ortho-stereogenicity (and ortho-diastereomeric relationships) can be discussed as above for the cases of Fig. 3.

3.1.3 Octahedral Complexes with [$\mathbf{Ma_2b_2cd}$]

Suppose that six achiral proligands (2a, 2b, c, and d) are placed on the six vertices of the reference octahedron skeleton **1** (the same as **3** in Fig. 2), where the substitution mode is represented by the following function:

$$f_3: \quad f_3(1)=\mathrm{a}, f_3(2)=\mathrm{b}, f_3(3)=\mathrm{c}, f_3(4)=\mathrm{b}, f_3(5)=\mathrm{d}, f_3(6)=\mathrm{a}. \tag{46}$$

This function is applied to the 15 reference stereoisograms shown in Fig. 2. The resulting 15 stereoisograms (Fig. 4) exhibit several sets of coincidence in accord with the previous result of combinatorial enumeration [10], which shows the presence of one achiral promolecule of $\mathbf{C}_{2v}$, one achiral promolecule of $\mathbf{C}'_s$, two achiral promolecules of $\mathbf{C}_s$, and two enantiomeric pairs of $\mathbf{C}_1$-promolecules (the partition-[2211]-row of Table 5 in [10]).

According to the IR-9.3.3.4 of the IUPAC recommendations 2005 [11], one promolecule of $\mathbf{C}_{2v}$ is characterized by the following configuration index:

135 *OC-6-12* ($\mathbf{C}_{2v}$) Stereoisogram **138** ($\mathbf{O}_{h\bar{1}\bar{1}}$) (Type IV), (47)

where the corresponding stereoisogram **138** belongs to Type IV, so that a quadruplet of promolecules is degenerated into the single promolecule **135** of $\mathbf{C}_{2v}$-symmetry.

The configuration index of one achiral promolecule of $\mathbf{C}'_s$ is obtained as follows:

141 *OC-6-22* ($\mathbf{C}'_s$) Stereoisogram **146** ($\mathbf{O}_{h\bar{1}\bar{1}}$(2 6)) (Type IV) (48)
(equivalent to Stereoisogram **162**)

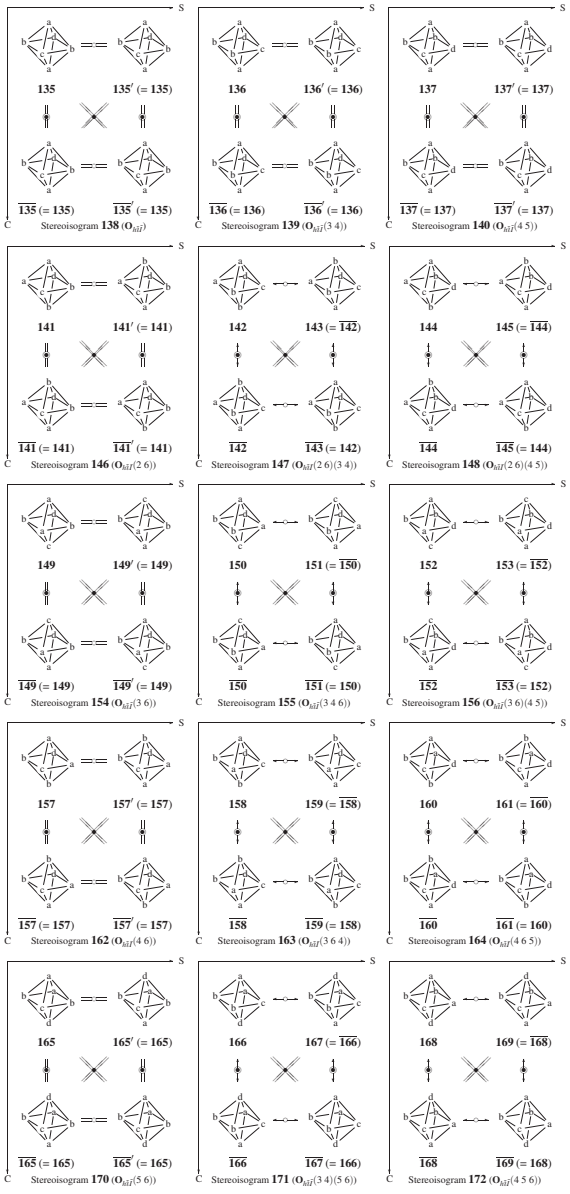


Figure 5: Multiplet of stereoisograms for representing stereoisomers (2 enantiomeric pairs and 4 achiral compounds) of octahedral complexes with [Ma$_2$b$_2$cd]. The CIP priority: a > b > c > d.

The stereoisogram **146** is equivalent to **162** under the action of a subgroup of the stereoisomeric group. Note that the subgroup corresponds to the subduction of a full symmetric [Ma_6] into [Ma_2b_2cd].

Two achiral promolecules of $\mathbf{C}_s$ are characterized by the following configuration indices:

136 *OC-6-14* ($\mathbf{C}_s$) Stereoisogram **139** ($\mathbf{O}_{h\bar{i}\bar{1}}(3\,4)$) (Type IV) (49)
(equivalent to Stereoisogram **140**)

149 *OC-6-43* ($\mathbf{C}_s$) Stereoisogram **154** ($\mathbf{O}_{h\bar{i}\bar{1}}(3\,6)$) (Type IV) (50)
(equivalent to Stereoisogram **170**)

Although the presence of two achiral promolecules of $\mathbf{C}_s$ was shown correctly in the partition-[2211]-row of Table 5 in [10], the structure of **27** in Fig. 2 of [10] was typeset incorrectly. It should be corrected as the structure **149**.

Each of the stereoisograms (**139** and **154**) exhibits equivalence under the action of a subgroup of the stereoisomeric group. The stereoisograms **139** and **140** (as well as **154** and **170**) shown in Fig. 5 are equivalent to each other so as to homomeric promolecules, which are identical under the action of the subgroup. Note again that the subgroup corresponds to the subduction of a full symmetric [Ma_6] into [Ma_2b_2cd].

The achiral promolecules (**135**, **136**, **141**, and **149**) are *RS*-astereogenic (or *RS*-non-stereogenic) under the action of the *RS*-permutation group (or the *RS*-stereogenic group, i.e., $\mathbf{O}_{\bar{i}}$) in accord with its stereoisogram of Type IV. The *RS*-astereogenic nature indicates that no *C/A*-descriptors are given to these promolecules.

On the other hand, each quadruplet of *RS*-stereoisomers (each stereoisogram, **138**, **139**, **146**, or **154**) is ortho-stereogenic under the action of the stereogenic group $\mathbf{S}^{[6]}$ (Eq. 16). Hence, these achiral promolecules (**135**, **136**, **141**, and **149**) are ortho-stereogenic according to Def. 1, although they are *RS*-astereogenic (or *RS*-non-stereogenic).

The two enantiomeric pairs of $\mathbf{C}_1$ are characterized by the following configuration indices with *A/C*-descriptors:

142 *OC-6-32-C*
143($=\overline{\mathbf{142}}$) *OC-6-32-A*
($\mathbf{C}_1$) Stereoisogram **147** ($\mathbf{O}_{h\bar{i}\bar{1}}(2\,6)(3\,4)$) (Type I) (51)
(equivalent to Stereoisograms **155**, **156**, and **164**)

144 *OC-6-42-A*
145($=\overline{\mathbf{144}}$) *OC-6-42-C*
($\mathbf{C}_1$) Stereoisogram **148** ($\mathbf{O}_{h\bar{i}\bar{1}}(2\,6)(4\,5)$) (Type I) (52)
(equivalent to Stereoisograms **163**, **171**, and **172**)

As for the $\mathbf{C}_1$-promolecules of Type I (**142** etc.) in Fig. 5, *RS*-stereogenicity (and *RS*-diastereomeric relationships) as well as ortho-stereogenicity (and ortho-diastereomeric relationships) can be discussed as above for the cases of Fig. 3.

3.1.4 Octahedral Complexes with Achiral Ligands of Other Constitutions

So long as we consider only achiral proligands as substituents, resulting promolecules belong to Type IV (achiral) or Type I (chiral). If they belong to Type IV, they are *RS*-astereogenic (or *RS*-non-stereogenic) under the action of the *RS*-permutation group (or the *RS*-stereogenic group, i.e., $\mathbf{O}_{\bar{i}}$), while they are ortho-stereogenic under the action of the stereogenic group $\mathbf{S}^{[6]}$ (Eq. 16).

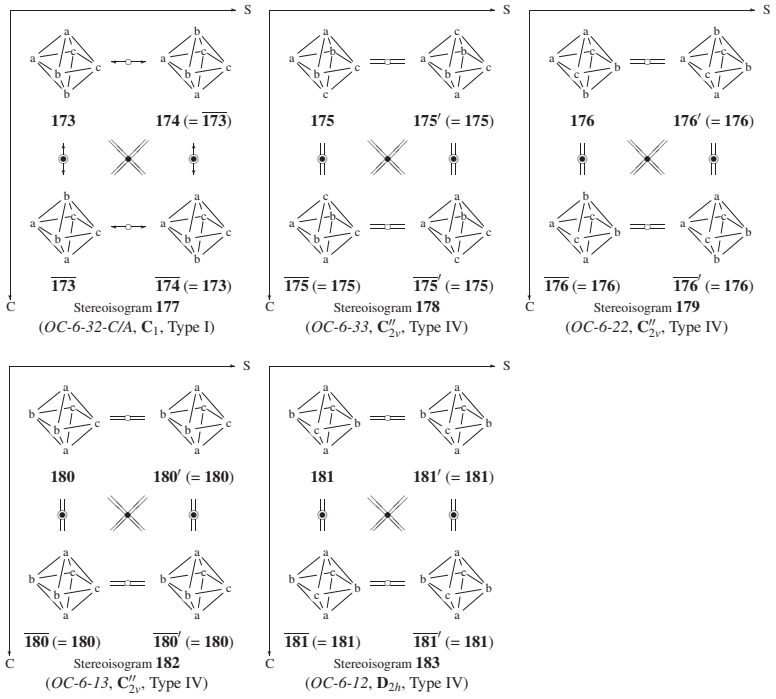


Figure 6: Stereoisomers of octahedral complexes with $[Ma_2b_2c_2]$. The configuration indices and *C/A*-descriptors are assigned by presuming the CIP priority a > b > c.

If resulting chiral promolecules belong to Type I, they are *RS*-stereogenic and ortho-stereogenic in the same way as the cases of Fig. 3.

As for octahedral complexes with $[Ma_2b_2c_2]$, six achiral proligands (2a, 2b, and 2c) are placed on the six vertices of the reference octahedron skeleton **1** (the same as **3** in Fig. 2). The substitution mode selected arbitrarily is represented by the following function:

$$f_4: \quad f_4(1) = \mathrm{a}, f_4(2) = \mathrm{a}, f_4(3) = \mathrm{b}, f_4(4) = \mathrm{c}, f_4(5) = \mathrm{c}, f_4(6) = \mathrm{b}, \tag{53}$$

which is applied to the 15 reference stereoisograms shown in Fig. 2. Among the resulting 15 stereoisograms, representatives are depicted in Fig. 6 in accord with the previous result of combinatorial enumeration [10]. The presence of one enantiomeric pair of $\mathbf{C}_1$ (Type I), three achiral promolecule of $\mathbf{C}''_{2v}$ (Type IV) and one achiral promolecule of $\mathbf{D}_{2h}$ (Type IV) has been shown in the partition-[222]-row of Table 5 of [10]. Their configuration indices and *C/A*-descriptors are assigned by presuming the CIP priority a > b > c.

The substitution of six achiral proligands (3a, b, c, and d) to the six vertices of the reference octahedron skeleton **1** (the same as **3** in Fig. 2) generates octahedral complexes with $[Ma_3bcd]$. According to the partition-[3111]-row of Table 5 in [10], there appear one enantiomeric pair of

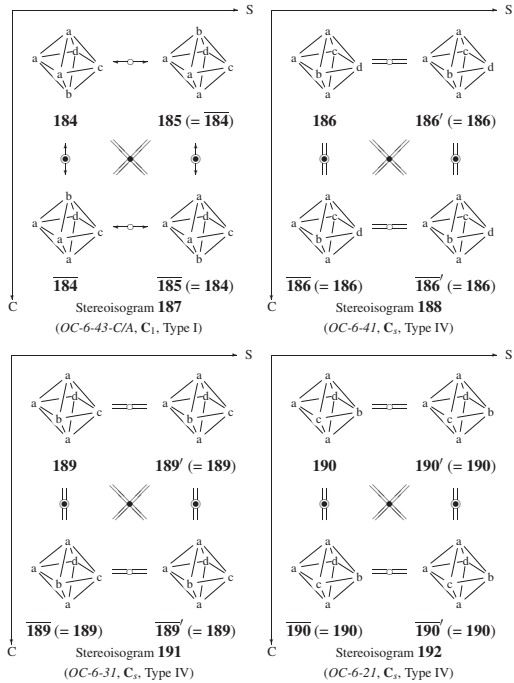


Figure 7: Stereoisomers of octahedral complexes with [Ma_3bcd]. The configuration indices and *C/A*-descriptors are assigned by presuming the CIP priority a > b > c > d.

$\mathbf{C}_1$ (Type I), three achiral promolecule of $\mathbf{C}''_{2v}$ (Type IV), and one achiral promolecule of $\mathbf{D}_{2h}$ (Type IV). The substitution mode is represented by the following function:

$$f_5: \quad f_5(1) = \mathrm{a}, f_5(2) = \mathrm{a}, f_5(3) = \mathrm{a}, f_5(4) = \mathrm{c}, f_5(5) = \mathrm{d}, f_5(6) = \mathrm{b}, \tag{54}$$

which is applied to the 15 reference stereoisograms (Fig. 2). By examining equivalence among the 15 resulting stereoisograms, representatives are selected in accord with the previous enumeration result [10], as depicted in Fig. 6. The configuration indices and *C/A*-descriptors are assigned by presuming the CIP priority a > b > c > d.

To examine octahedral complexes with [Ma_3b_2c], six achiral proligands (3a, 2b, and c) are placed on the six vertices of the reference octahedron skeleton **1** (the same as **3** in Fig. 2), where the substitution mode is represented by the following function:

$$f_6: \quad f_6(1) = \mathrm{a}, f_6(2) = \mathrm{a}, f_6(3) = \mathrm{a}, f_6(4) = \mathrm{b}, f_6(5) = \mathrm{c}, f_6(6) = \mathrm{b}. \tag{55}$$

This function is applied to the 15 reference stereoisograms (Fig. 2) to give 15 stereoisograms, which are examined to give equivalence classes by referring to the previous result of combinatorial enumeration [10]. The representatives selected from the resulting 15 stereoisograms are

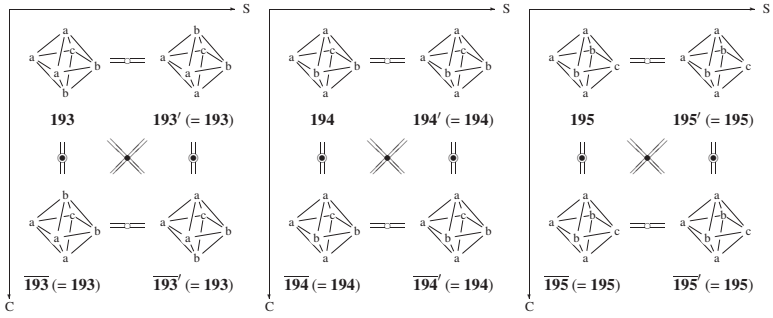


Figure 8: Stereoisomers of octahedral complexes with $[Ma_3b_2c]$. The configuration indices are assigned by presuming the CIP priority a > b > c.

all Type IV stereoisograms and depicted in Fig. 8, i.e., one achiral promolecule of $\mathbf{C}'_s$ and two achiral promolecule of $\mathbf{C}_s$ (cf. the partition-[321]-row of Table 5 in [10]). Their configuration indices are assigned by presuming the CIP priority a > b > c. No *C/A*-descriptors are assigned.

As for octahedral complexes with $[Ma_3b_3]$, six achiral proligands (3a and 3b) are placed on the six vertices of the reference octahedron skeleton **1** (the same as **3** in Fig. 2) according to the following function:

$$f_7 : \quad f_7(1) = \mathrm{a}, f_7(2) = \mathrm{a}, f_7(3) = \mathrm{a}, f_7(4) = \mathrm{b}, f_7(5) = \mathrm{b}, f_7(6) = \mathrm{b}, \tag{56}$$

which is applied to the 15 reference stereoisograms shown in Fig. 2. The equivalence between the resulting 15 stereoisograms is examined so as to leave two representatives depicted in Fig. 9, which are both Type IV stereoisograms. They are consistent with the previous enumeration result [10], which shows the presence of one achiral promolecule of $\mathbf{C}_{3v}$ and one achiral promolecule of $\mathbf{C}_{2v}$ (cf. the partition-[33]-row of Table 5 in [10]). The configuration indices are assigned by presuming the CIP priority a > b. No *A/C*-descriptors are assigned.

To examine octahedral complexes with $[Ma_4bc]$, six achiral proligands (4a, b, and c) are placed on the six vertices of the reference octahedron skeleton **1** (the same as **3** in Fig. 2), where the substitution mode is represented by the following function:

$$f_8 : \quad f_8(1) = \mathrm{a}, f_8(2) = \mathrm{a}, f_8(3) = \mathrm{b}, f_8(4) = \mathrm{a}, f_8(5) = \mathrm{c}, f_8(6) = \mathrm{a}. \tag{57}$$

This function is applied to the 15 reference stereoisograms (Fig. 2) to give 15 stereoisograms, from which one achiral promolecule of $\mathbf{C}_{4v}$ (Type IV) and one achiral promolecule of $\mathbf{C}_s$ (Type IV) are selected as representatives. They are depicted in Fig. 10. The number of these promolecules is consistent with the previous result of combinatorial enumeration (the partition-[411]-row of Table 5 in [10]). The configuration indices are assigned by presuming the CIP priority a > b > c. No *A/C*-descriptors are assigned.

Six achiral proligands (4a and 2b) are placed on the six vertices of the reference octahedron skeleton **1** (the same as **3** in Fig. 2) so as to give octahedral complexes with $[Ma_4b_2]$. A substitution mode selected arbitrarily is represented by the following function:

$$f_9 : \quad f_9(1) = \mathrm{a}, f_9(2) = \mathrm{a}, f_9(3) = \mathrm{b}, f_9(4) = \mathrm{a}, f_9(5) = \mathrm{b}, f_9(6) = \mathrm{a}, \tag{58}$$

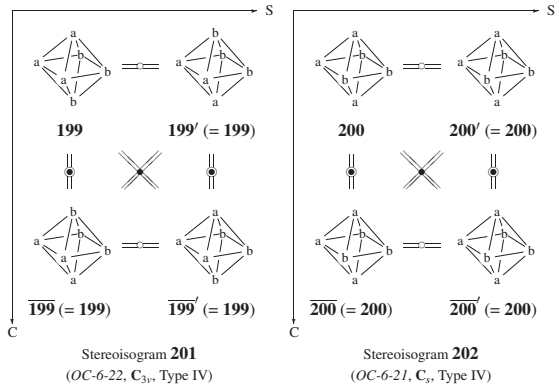


Figure 9: Stereoisomers of octahedral complexes with $[Ma_3b_3]$. The configuration indices are assigned by presuming the CIP priority a $>$ b.

which is applied to the 15 reference stereoisograms shown in Fig. 2. The resulting 15 stereoisograms (omitted) contain some duplications in accord with the previous result of combinatorial enumeration [10], which shows the presence of one achiral promolecule of $\mathbf{D}_{4h}$ (Type IV) and one achiral promolecule of $\mathbf{C}''_{2v}$ (Type IV) in the partition-[42]-row of Table 5 [10]. Two representatives selected from the resulting 15 stereoisograms are depicted in Fig. 11, where the configuration indices are assigned by presuming the CIP priority a $>$ b. No *A/C*-descriptors are assigned.

As reported previously in the partition-[51]-row of Table 5 [10], there is one achiral promolecule with $[Ma_5b]$, which belongs to $\mathbf{C}_{4v}$. This promolecule is *RS*-astereogenic and astereogenic so as to give no stereoisomers. The corresponding stereoisogram exhibits a Type IV character, although it is omitted.

One achiral promolecule with $[Ma_6]$ belongs to $\mathbf{O}_h$, as reported previously in the partition-[6]-row of Table 5 [10]. This promolecule is *RS*-astereogenic and astereogenic so as to give no stereoisomers. The corresponding stereoisogram exhibits a Type IV character, although it is omitted.

It should be noted that Quotation 1 is also effective, so long as we consider only achiral proligands as substituents. If resulting chiral promolecules belong to Type I, the definition of Quotation 1 teaches us that the central atom is "stereogenic" so as to be a "chiral" center. This can explain the capability of giving *A/C*-descriptors. If resulting achiral promolecules belong to Type IV, on the other hand, the definition of Quotation 1 teaches us that the central atom is "stereogenic", but not to be a "chiral" center. This can explain the incapability of giving *A/C*-descriptors. Thus, the conventional stereochemistry (e.g., Quotation 1) turns out to rely on a methodology that successful cases in which only achiral proligands are considered as substituents are unreasonably applied to other general cases which require more sophisticated treatments. The stereoisogram approach provides us with a more reliable methodology for treating such sophisticated cases, as discussed in the following subsection.

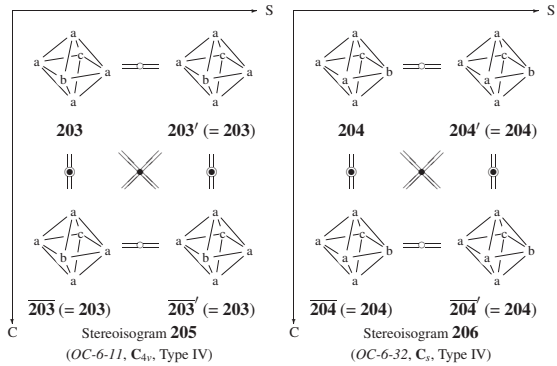


Figure 10: Stereoisomers of octahedral complexes with [Ma$_4$bc]. The configuration indices are assigned by presuming the CIP priority a $>$ b $>$ c.

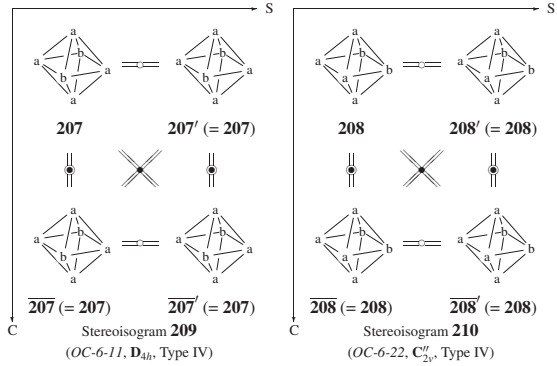


Figure 11: Stereoisomers of octahedral complexes with [Ma$_4$b$_2$]. The configuration indices are assigned by presuming the CIP priority a $>$ b.

3.2 Stereoisomers of Octahedral Complexes with Chiral and Achiral Proligands

In the preceding subsection, we take account of only achiral (pro)ligands as substituents of octahedral complexes, where there have emerged stereoisograms of Type I and IV. In this subsection, we take account of chiral (pro)ligands as substituents along with achiral (pro)ligands. Thereby, there additionally emerge stereoisograms of Type II, III, and V, so as to exhibit more-complicated features, which have been overlooked or exceptionally treated in the conventional stereochemistry.

3.2.1 Octahedral Complexes with $[Ma_2bcp_2]$ or $[Ma_2bc\overline{p}_2]$

Let us examine four achiral proligands (2a, b, and c) and two chiral proligands (2p or 2$\overline{\text{p}}$) as a set of substituents for the six vertices of the reference octahedron skeleton **1** (the same as **3** in Fig. 2), where p and $\overline{\text{p}}$ represent enantiomeric proligands of a pair. Then, the substitution mode is represented by the following function:

$$f_{10}: \quad f_{10}(1)=\text{a}, f_{10}(2)=\text{b}, f_{10}(3)=\text{p}, f_{10}(4)=\text{c}, f_{10}(5)=\text{p}, f_{10}(6)=\text{a}, \tag{59}$$

which is applied to the 15 reference stereoisograms shown in Fig. 2. Thereby, there appear 15 stereoisograms (Fig. 12), which coincide to generate promolecules as equivalence classes under the action of the stereoisomeric group. Such promolecules have already enumerated combinatorially to be one enantiomeric pair of chiral promolecules of $\mathbf{C}_2$ and seven enantiomeric pairs of chiral promolecules of $\mathbf{C}_1$ as shown in the partition-[211;2]-row of Table 7 [10].

One enantiomeric pair of chiral promolecules of $\mathbf{C}_2$ is represented by the stereoisogram of Type II, i.e., **214** of Fig. 12, the quadruplet of which is degenerated into a pair of enantiomers as follows:

$$\left.\begin{array}{ll} \mathbf{211} & \textit{OC-6-13} \\ \overline{\mathbf{211}} & \textit{OC-6-13} \end{array}\right\} \quad (\mathbf{C}_2) \quad \text{Stereoisogram } \mathbf{214}\ (\mathbf{O}_{h\tilde{i}\tilde{I}}) \text{ (Type II).} \tag{60}$$

The configuration indices are assigned by presuming the CIP priority a > b > c > p (for **211**) or a > b > c > $\overline{\text{p}}$ (for $\overline{\mathbf{211}}$) according to the IR-9.3.3.4 of the IUPAC recommendations 2005 [11]. The *C/A*-descriptors are not assigned because of *RS*-astereogenicity (or *RS*-non-stereogenicity) due to the stereoisogram of Type II, i.e., **211** = **211**′.

Note that the chirality of **211** (or $\overline{\mathbf{211}}$) has nothing to do with the impossibility of giving *C/A*-descriptors. In other words, this Type II case is a counterexample of Quotation 2 described in the Introduction, if our discussion is restricted to the stereoisogram **214**. Thus, the chiral center of **211** (or $\overline{\mathbf{211}}$) in a purely geometric meaning is not *RS*-stereogenic according to Def. 2.

However, a broader consideration should be developed, if our discussion is extended to cover relationships between the stereoisogram **214** and other stereoisograms collected in Fig. 12. Thus, the stereoisogram **214** for **211** (and $\overline{\mathbf{211}}$) is ortho-stereogenic according to Def. 1 as well as the enantiomeric pair of **211**/$\overline{\mathbf{211}}$ is stereogenic according to Def. 3. Note that the chirality of **211** (or $\overline{\mathbf{211}}$), again, has nothing to do with Def. 1 and Def. 3.

In summary, the center of **211** (or $\overline{\mathbf{211}}$) is chiral (in a purely geometric meaning), not *RS*-stereogenic (*RS-a*stereogenic, Def. 2), ortho-stereogenic (Def. 1), and stereogenic (Def. 3). The incapability of giving *C/A*-descriptors depends upon the *RS-a*stereogenic property due to Def. 2. The capability of giving stereoisomers depends upon the stereogenicity due to Def. 3 and, more definitely speaking, upon the ortho-stereogenicity due to Def. 1.

Three of the seven enantiomeric pairs of chiral promolecules of $\mathbf{C}_1$ are characterized by the stereoisograms of Type II, i.e., **215** (equivalent to **216**), **222** (equivalent to **238**), and **230** (equivalent to **246**) of Fig. 12, each quadruplet of which is degenerated into a pair of enantiomers as follows:

$$\left.\begin{array}{ll} \mathbf{212} & \textit{OC-6-14} \\ \overline{\mathbf{212}} & \textit{OC-6-14} \end{array}\right\} \quad (\mathbf{C}_1) \quad \text{Stereoisogram } \mathbf{215}\ (\mathbf{O}_{h\tilde{i}\tilde{I}}(3\ 4)) \text{ (Type II),} \tag{61}$$

(equivalent to Stereoisogram **216**)

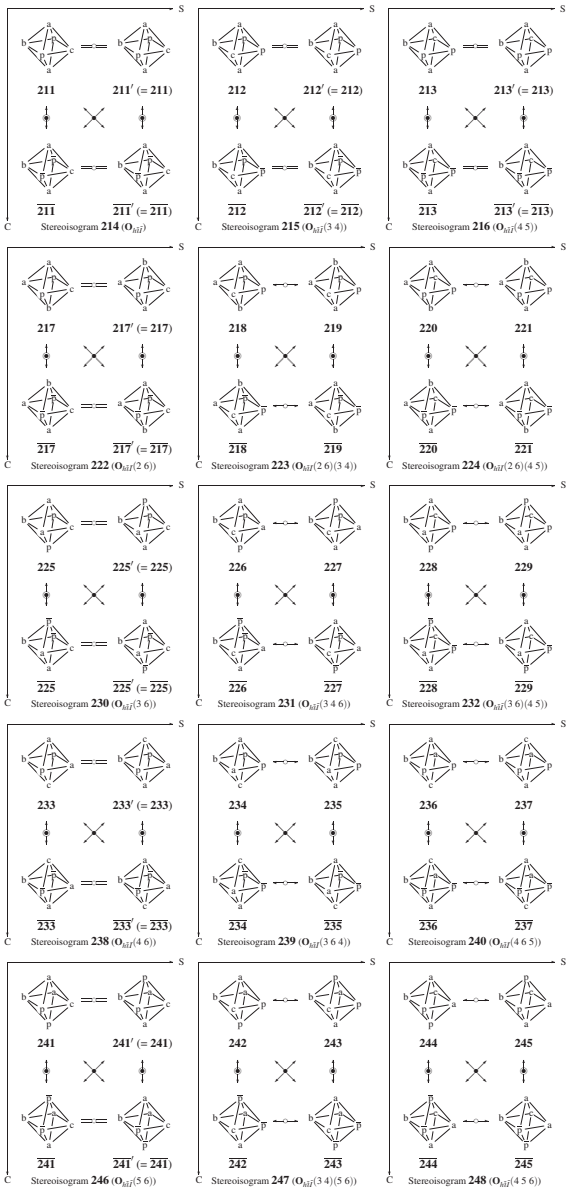


Figure 12: Multiplet of stereoisomers of octahedral complexes with [Ma_2bcp_2] or [$Ma_2bc\overline{p}_2$]. The CIP priority: a > b > c > p or a > b > c > $\overline{p}$.

$$\left.\begin{array}{ll} \mathbf{217} & \textit{OC-6-32} \\ \overline{\mathbf{217}} & \textit{OC-6-32} \end{array}\right\} \quad (\mathbf{C}_1) \quad \text{Stereoisogram } \mathbf{222}\ (\mathbf{O}_{h\tilde{i}\tilde{I}}(2\ 6))\ \text{(Type II)}, \tag{62}$$

(equivalent to Stereoisogram **238**)

$$\left.\begin{array}{ll} \mathbf{225} & \textit{OC-6-44} \\ \overline{\mathbf{225}} & \textit{OC-6-44} \end{array}\right\} \quad (\mathbf{C}_1) \quad \text{Stereoisogram } \mathbf{230}\ (\mathbf{O}_{h\tilde{i}\tilde{I}}(3\ 6))\ \text{(Type II)}, \tag{63}$$

(equivalent to Stereoisogram **246**)

To conduct a more rational naming on the basis of the stereoisogram approach, we should consider a common CIP priority sequence: $a > b > c > p > \overline{p}$ so that the priority 4 is assigned to p, while the priority 5 is assigned to $\overline{p}$. Thereby, we can assign a pair of names: *OC-6-14* for **212** and *OC-6-15* for $\overline{\mathbf{212}}$ (Eq. 61); as well as *OC-6-44* for **225** and *OC-6-55* for $\overline{\mathbf{225}}$ (Eq. 63).

On the same line as Eq. 60 for a Type II case, Eqs. 61–63 indicate that the respective Type II cases are characterized as being chiral (in a purely geometric meaning), not *RS*-stereogenic (*RS-a*stereogenic, Def. 2), ortho-stereogenic (Def. 1), and stereogenic (Def. 3). Again, the incapability of giving *C/A*-descriptors depends upon the *RS-a*stereogenic property due to Def. 2 as well as the capability of giving stereoisomers depends upon the stereogenicity due to Def. 3 and, more definitely speaking, upon the ortho-stereogenicity due to Def. 1.

The remaining four of the seven enantiomeric pairs of chiral promolecules ($\mathbf{C}_1$) are characterized by two stereoisograms of Type III. One is the stereoisogram **223** (equivalent to **224**, **231**, and **248**) for two enantiomeric pairs and the other is the stereoisogram **232** for two enantiomeric pairs (equivalent to **239**, **240**, and **247**).

On one hand for the former stereoisogram (**223**), the configuration indices with *C/A*-descriptors are assigned as follows according to the IR-9.3.3.4 and IR-9.3.4.8 of the IUPAC recommendations 2005 [11]:

$$\left.\begin{array}{ll} \mathbf{218} & \textit{OC-6-42-C} \\ \mathbf{219} & \textit{OC-6-42-A} \\ \overline{\mathbf{218}} & \textit{OC-6-42-A} \\ \overline{\mathbf{219}} & \textit{OC-6-42-C} \end{array}\right\} \quad (\mathbf{C}_1) \quad \text{Stereoisogram } \mathbf{223}\ (\mathbf{O}_{h\tilde{i}\tilde{I}}(2\ 6)(3\ 4))\ \text{(Type III)} \tag{64}$$

(equivalent to Stereoisograms **224**, **231**, and **248**)

Although the practices of giving the *C/A*-descriptors in the present stereoisogram approach are the same as the conventions of stereochemistry, their theoretical bases are different from each other. Thus, in the present stereoisogram approach, the *RS*-diastereomers **218/219** (different from such enantiomers **218/**$\overline{\mathbf{218}}$ as postulated in the conventional stereochemistry) are considered to be pairwise named, i.e., *OC-6-42-C* for **218** and *OC-6-42-A* for **219**, where the CIP priority is presumed to be $a > b > c > p$. On the same line, the *RS*-diastereomers $\overline{\mathbf{218}}$/$\overline{\mathbf{219}}$ are pairwise named to be *OC-6-42-A* for $\overline{\mathbf{218}}$ and *OC-6-42-C* for $\overline{\mathbf{219}}$, where the CIP priority is presumed to be $a > b > c > \overline{p}$. Note that each pair of the *C/A*-descriptors is found not to be assigned to a pair of enantiomers by judging from the different CIP priorities applied, i.e., $a > b > c > p$ vs. $a > b > c > \overline{p}$, where the CIP priority of the former series assigns 4 to p, while the CIP priority of the latter series assigns 4 to $\overline{p}$. It follows that the configuration indices turn out to be seemingly identical.

To conduct a more rational naming on the basis of the stereoisogram approach, we should consider a common CIP priority sequence: $a > b > c > p > \overline{p}$ so that the priority 4 is assigned

to p, while the priority 5 is assigned to $\overline{\mathrm{p}}$. Thereby, we can assign a pair of names: *OC-6-42-C* for **218** and *OC-6-42-A* for **219**; as well as another pair of names: *OC-6-52-A* for $\overline{\mathbf{218}}$ and *OC-6-52-C* for $\overline{\mathbf{219}}$.

On the other hand for the latter stereoisogram (**232**), a parallel treatment to the preceding paragraphs gives the following result:

$$\left.\begin{array}{ll} \mathbf{228} & \textit{OC-6-43-C} \\ \mathbf{229} & \textit{OC-6-43-A} \\ \overline{\mathbf{228}} & \textit{OC-6-43-A} \\ \overline{\mathbf{229}} & \textit{OC-6-43-C} \end{array}\right\}\Bigg\} \quad (\mathbf{C}_1) \quad \text{Stereoisogram } \mathbf{232}\ (\mathbf{O}_{h\bar{i}\bar{I}}(3\ 6)(4\ 5))\ \text{(Type III)} \qquad (65)$$

(equivalent to Stereoisograms **239**, **240**, and **247**)

Again, each pair of the *C/A*-descriptors is found to be assigned to a pair of *RS*-diastereomers, but not to a pair of enantiomers by judging from the different CIP priorities applied.

By applying a common CIP priority sequence ($\mathrm{a} > \mathrm{b} > \mathrm{c} > \mathrm{p} > \overline{\mathrm{p}}$) to the *RS*-stereoisomers (Stereoisogram **232**), we are able to assign a pair of more rational names, i.e., *OC-6-43-C* for **228** and *OC-6-43-A* for **229**; as well as another pair of more rational names: *OC-6-53-A* for $\overline{\mathbf{228}}$ and *OC-6-53-C* for $\overline{\mathbf{229}}$.

Equations 64 and 65 indicate that the respective Type III cases are characterized as being chiral (in a purely geometric meaning), *RS*-stereogenic (Def. 2), ortho-stereogenic (Def. 1), and stereogenic (Def. 3). It should be emphasized that *RS*-stereogenicity (Def. 2), ortho-stereogenicity (Def. 1), and stereogenicity (Def. 3) are conceptually different from chirality for deciding enantiomeric relationships. In fact, the *RS*-stereogenicity (Def. 2), the ortho-stereogenicity (Def. 1), and the stereogenicity (Def. 3) are assigned to **218** etc. and separately to $\overline{\mathbf{218}}$ etc., where the enantiomeric relationships between **218** and $\overline{\mathbf{218}}$, etc. have nothing to do with the assignments by Defs. 1–3. As a result, the second sentence of Quotation 1 in the Introduction is incapable of explaining these Type III cases rationally.

3.2.2 Octahedral Complexes with [$\mathrm{Ma_2bcp\overline{p}}$]

Consider a set of four achiral proligands (2a, b, and c) and an enantiomeric pair of chiral proligands (p and $\overline{\mathrm{p}}$) to generate octahedral complexes with [$\mathrm{Ma_2bcp\overline{p}}$]. The set of proligands is placed on the six vertices of the reference octahedron skeleton **1** (the same as **3** in Fig. 2), where the substitution mode is represented by the following function:

$$f_{11}: \quad f_{11}(1)=\mathrm{a}, f_{11}(2)=\mathrm{b}, f_{11}(3)=\mathrm{p}, f_{11}(4)=\mathrm{c}, f_{11}(5)=\overline{\mathrm{p}}, f_{11}(6)=\mathrm{a}. \qquad (66)$$

After this function is applied to the 15 reference stereoisograms shown in Fig. 2, the resulting 15 stereoisograms (Fig. 12) are examined from a viewpoint of equivalence under the stereoisomeric group. They are categorized into equivalence classes in accord with the previous result of combinatorial enumeration [10]. Thereby, we are able to confirm the presence of three achiral promolecules of $\mathbf{C}_s$, two achiral promolecules of $\mathbf{C}'_s$, and five enantiomeric pairs of chiral promolecules of $\mathbf{C}_1$ (the partition-[211;11]-row of Table 7 in [10]).

One achiral promolecule of $\mathbf{C}_s$ is represented by the stereoisogram of Type IV, i.e., **252** of Fig. 13, the quadruplet of which is degenerated into a single molecule as follows:

$$\mathbf{249}\ \ \textit{OC-6-13} \quad (\mathbf{C}_s) \quad \text{Stereoisogram } \mathbf{252}\ (\mathbf{O}_{h\bar{i}\bar{I}})\ \text{(Type IV)}. \qquad (67)$$

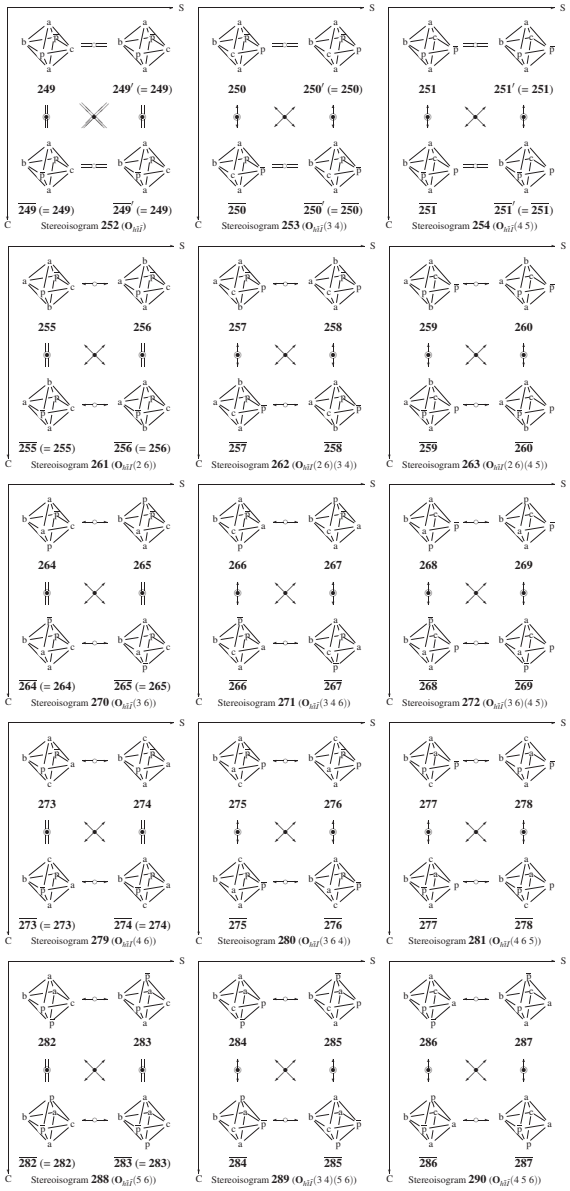


Figure 13: Multiplet of stereoisomers of octahedral complexes with [$Ma_2bcp\overline{p}$]. The CIP priority: a > b > c > p > $\overline{p}$.

The configuration index is assigned by presuming the CIP priority a > b > c > p > $\overline{\text{p}}$ according to the IR-9.3.3.4 of the IUPAC recommendations 2005 [11]. In terms of the stereoisogram of Type IV, *C/A*-descriptors are not assigned because of *RS*-astereogenicity (i.e., **249** = **249**′), not because of achirality (i.e., **249** = $\overline{\mathbf{249}}$).

The remaining two promolecules of $\mathbf{C}_s$ construct a stereoisogram of Type V, i.e., **261** (equivalent to **238**) of Fig. 12, the quadruplet of which is degenerated into a pair of *RS*-diastereomers as follows:

$$\left.\begin{array}{ll} \mathbf{255} & \textit{OC-6-32-C} \\ \mathbf{256} & \textit{OC-6-32-A} \end{array}\right\} \quad (\mathbf{C}_s) \quad \text{Stereoisogram } \mathbf{261}\ (\mathbf{O}_{h\bar{i}\bar{I}}(2\ 6))\ \text{(Type V)}. \qquad (68)$$

(equivalent to Stereoisogram **279**)

The configuration indices are assigned by presuming the CIP priority a > b > c > p > $\overline{\text{p}}$ according to the IR-9.3.3.4 of the IUPAC recommendations 2005 [11]. Although **255** and **256** are achiral, *C/A*-descriptors are pairwise assigned to the pair of the *RS*-diastereomers (**255** and **256**), where the naming of *C/A*-descriptors is conducted according to the IR-9.3.4.8 of the IUPAC recommendations 2005 [11]. It should be emphasized that the achirality of **255** and **256** indicates the absence of enantiomers, as found by the stereoisogram **261**. As a result, the *C/A*-descriptors due to the IR-9.3.4.8 of the IUPAC recommendations 2005 [11] by no means differentiate an enantiomeric relationship, which is absent in each of the achiral promolecules (**255** and **256**) as well as between them. This point have been be discussed from a viewpoint of chirality faithfulness in Part I of this series.

Note that each of *RS*-diastereomers (**255** and **256**) is counted once by the USCI approach [10]. Hence, the stereoisogram of Type IV (**252** of Fig. 12, cf. Eq. 67) and the stereoisogram of Type V (**261** of Fig. 12, cf. Eq. 68) rationalize the presence of three $\mathbf{C}_s$-promolecules (**249**, **255**, and **256**).

Two promolecules of $\mathbf{C}_s'$ construct a stereoisogram of Type V, i.e., **270** (equivalent to **246**) of Fig. 12, the quadruplet of which is degenerated into a pair of *RS*-diastereomers as follows:

$$\left.\begin{array}{ll} \mathbf{264} & \textit{OC-6-54-A} \\ \mathbf{265} & \textit{OC-6-54-C} \end{array}\right\} \quad (\mathbf{C}_s') \quad \text{Stereoisogram } \mathbf{270}\ (\mathbf{O}_{h\bar{i}\bar{I}}(3\ 6))\ \text{(Type V)}, \qquad (69)$$

(equivalent to Stereoisogram **288**)

The configuration indices and the *C/A*-descriptors can be discussed along the same line as Stereoisogram **261** of Type V. Note again that each of the *RS*-diastereomers (**264** and **265**) is counted once by the USCI approach [10]. Hence, the stereoisogram of Type V (**270** of Fig. 12, cf. Eq. 69) rationalizes the presence of two $\mathbf{C}_s'$-promolecules, i.e., **264** and **265**.

Equations 68 and 69 indicate that the Type V cases are characterized as being achiral (in a purely geometric meaning), *RS*-stereogenic (Def. 2), ortho-stereogenic (Def. 1), and stereogenic (Def. 3). It should be emphasized, again, that *RS*-stereogenicity (Def. 2), ortho-stereogenicity (Def. 1), and stereogenicity (Def. 3) are conceptually different from the concept of chirality, because of achirality (self-enantiomeric relationships) in these Type V cases. Although such Type V cases (as well as by Type I and IV cases) seem to support the conventional stereochemistry by satisfying Quotation 1, they have in turn caused confusions to Types II and III cases described in the Introduction.

One enantiomeric pair among the five enantiomeric pairs of $\mathbf{C}_1$ is characterized by the stereoisogram of Type II, i.e., **253** (equivalent to **254**), each quadruplet of which is degener-

ated into a pair of enantiomers as follows:

$$\left.\begin{array}{ll} \mathbf{250} & \textit{OC-6-14} \\ \overline{\mathbf{250}} & \textit{OC-6-15} \end{array}\right\} \quad (\mathbf{C}_1) \quad \text{Stereoisogram } \mathbf{253}\ (\mathbf{O}_{h\bar{i}\bar{I}}(3\ 4))\ \text{(Type II)}, \tag{70}$$

(equivalent to Stereoisogram **254**)

The configuration indices (*OC-6-14* for **250** and *OC-6-15* for $\overline{\mathbf{250}}$) are assigned by presuming the same CIP priority $\mathrm{a} > \mathrm{b} > \mathrm{c} > \mathrm{p} > \overline{\mathrm{p}}$. However, *C/A*-descriptors cannot be assigned because of the *RS*-astereogenicity of the corresponding Type II stereoisogram (**253**). The configuration indices (without *C/A*-descriptors) are not paired in spite of the enantiomeric relationship between **250** and $\overline{\mathbf{250}}$. This case will be discussed again in detail.

The remaining four among the five enantiomeric pairs of chiral promolecules ($\mathbf{C}_1$) are characterized by two stereoisograms of Type III. One is the stereoisogram **262** (equivalent to the stereoisograms **263**, **271**, and **290**) for two enantiomeric pairs and the other is the stereoisogram **272** (equivalent to the stereoisograms **280**, **281**, and **289**) for the remaining two enantiomeric pairs.

On one hand for the former stereoisogram (**262**), the configuration indices with *C/A*-descriptors are assigned as follows:

$$\left.\begin{array}{l} \left.\begin{array}{ll} \mathbf{257} & \textit{OC-6-42-C} \\ \mathbf{258} & \textit{OC-6-42-A} \\ \overline{\mathbf{257}} & \textit{OC-6-52-A} \\ \overline{\mathbf{258}} & \textit{OC-6-52-C} \end{array}\right\} \end{array}\right\} \quad (\mathbf{C}_1) \quad \text{Stereoisogram } \mathbf{262}\ (\mathbf{O}_{h\bar{i}\bar{I}}(2\ 6)(3\ 4))\ \text{(Type III)} \tag{71}$$

(equivalent to Stereoisograms **263**, **271**, and **290**)

Although the practices of giving the *C/A*-descriptors are done according to the IR-9.3.3.4 and IR-9.3.4.8 of the IUPAC recommendations 2005 [11], the present stereoisogram approach is based on a theoretical foundation different from the conventional stereochemistry. Thus, in the present stereoisogram approach, the *RS*-diastereomers **257/258** (different from such enantiomers as postulated in the conventional stereochemistry, i.e., **257**/$\overline{\mathbf{257}}$) are considered to be pairwise named, i.e., *OC-6-42-C* for **257** and *OC-6-42-A* for **258**, where the CIP priority is presumed to be $\mathrm{a} > \mathrm{b} > \mathrm{c} > \mathrm{p} > \overline{\mathrm{p}}$. On the same line, the *RS*-diastereomers $\overline{\mathbf{257}}/\overline{\mathbf{258}}$ are pairwise named to have *OC-6-52-A* for $\overline{\mathbf{257}}$ and *OC-6-52-C* for $\overline{\mathbf{258}}$. Although each pair of the *C/A*-descriptors seems to be pairwise assigned to a pair of enantiomers, two enantiomers of each pair are not paired because they are different in their configuration indices, where the same CIP priority (i.e., $\mathrm{a} > \mathrm{b} > \mathrm{c} > \mathrm{p} > \overline{\mathrm{p}}$) is applied.

On the other hand for the latter stereoisogram (**272**), a parallel treatment to the preceding paragraph gives the following result:

$$\left.\begin{array}{l} \left.\begin{array}{ll} \mathbf{268} & \textit{OC-6-43-C} \\ \mathbf{269} & \textit{OC-6-43-A} \\ \overline{\mathbf{268}} & \textit{OC-6-53-A} \\ \overline{\mathbf{269}} & \textit{OC-6-53-C} \end{array}\right\} \end{array}\right\} \quad (\mathbf{C}_1) \quad \text{Stereoisogram } \mathbf{272}\ (\mathbf{O}_{h\bar{i}\bar{I}}(3\ 6)(4\ 5))\ \text{(Type III)} \tag{72}$$

(equivalent to Stereoisograms **280**, **281**, and **289**)

Again, each pair of the *C/A*-descriptors is decided to be assigned to a pair of *RS*-diastereomers, but not to a pair of enantiomers by judging their configuration indices.

3.3 Extension of Stereoisomeric Groups

Because chiral ligands p and $\overline{\mathrm{p}}$ are enantiomeric in isolation, the stereoisomers having a_2bcp_2 or $a_2bc\overline{p}_2$ (Fig. 12) and the stereoisomers having $a_2bcp\overline{p}$ (Fig. 13) are stereoisomeric to each other, if stereoisomerism means the convertibility into a common graph. Strictly speaking, they have been separately assigned to the stereoisomeric group $\mathbf{S}^{[6]}_{\mathbf{O}_{h\bar{i}\bar{I}}}$ (Eq. 17) by means of the stereoisogram approach at the present stage. It follows that the stereoisomeric group $\mathbf{S}^{[6]}_{\mathbf{O}_{h\bar{i}\bar{I}}}$ (Eq. 17) should be further extended so as to cover both the series of stereoisomers (Figs. 12 and 13). Such an extended stereoisomeric group should treat a multi-centered skeleton having two or more *RS*-stereogenic centers, as suggested by an article concerned with theory of organic stereoisomerism [13]. This extension is open to further investigation.

4 Stereogenicity and Stereoisomerism

In this section, the conventional terms "stereogenicity" and "stereoisomerism" are discussed in order to be harmonized with the terms *RS-stereogenicity* and *RS-stereoisomerism* of the present stereoisogram approach.

4.1 *RS*-Stereogenicity and Stereogenicity

In Subsection 2.2, the terminology of the stereoisogram approach has been discussed mainly from a viewpoint of relational terms. In this subsection, the terminology is discussed from a viewpoint of attributive terms.

4.1.1 Attributive Terms vs. Relational Terms

The construction of the stereoisomeric group $\mathbf{S}^{[6]}_{\mathbf{O}_{h\bar{i}\bar{I}}}$ (Eq. 17) by starting from the symmetric group of degree 6 ($\mathbf{S}_{[6]}$) and the *RS*-stereoisomeric group $\mathbf{O}_{h\bar{i}\bar{I}}$ (Eq. 1 or Eq. 2) provides us a hint to differentiate the term *stereogenicity* (cf. Def. 3) from *RS*-stereogenicity (cf. Def. 2). For the sake of avoiding complexity, we here take account of the stereoisomeric group $\mathbf{S}^{[6]}_{\mathbf{O}_{h\bar{i}\bar{I}}}$ (Eq. 17), which is concerned with a single *RS*-stereogenic center.

When the permutation part $\mathbf{S}^{[6]}$ (Eq. 16), which is contained in the stereoisomeric group $\mathbf{S}^{[6]}_{\mathbf{O}_{h\bar{i}\bar{I}}}$ (Eq. 17), operates onto a promolecule derived from the octahedral skeleton (**1**), there appears a set of stereoisomers with maintaining the configurations of proligands (in isolation). In other words, rotoreflection operations are not involved in $\mathbf{S}^{[6]}$ (Eq. 16), where enantiomeric relationships are not taken into consideration.

Because the $\mathbf{S}^{[6]}$ contains the *RS*-permutation group (or *RS*-stereogenic group, i.e., $\mathbf{O}_{\bar{I}}$ shown by Eq. 15) as a subgroup, the permutations involved in $\mathbf{S}^{[6]}$ are categorized into 15 cosets, as shown in Eq. 16. The representatives of these cosets are used to construct the stereoisomeric group $\mathbf{S}^{[6]}_{\mathbf{O}_{h\bar{i}\bar{I}}}$ (Eq. 17). As found by the mode of construction (Eq. 16 vs. Eq. 17), the 15 cosets of $\mathbf{S}^{[6]}_{\mathbf{O}_{h\bar{i}\bar{I}}}$ (Eq. 17) converted into one another (or fixed) by the action of rotations which contained in the $\mathbf{S}^{[6]}$. According to these conversions, a quadruplet of *RS*-stereoisomers (a stereoisogram) is converted into stereoisomeric quadruplets (stereoisograms). This convertibility is referred to as *ortho-stereogenicity* (cf. Def. 1).

When we focus our attention on an enantiomeric pair, it is converted into another enantiomeric pair by the action of rotations which contained in the $\mathbf{S}^{[6]}$. This convertibility is referred to as *stereogenicity* (cf. Def. 3).

It should be noted that stereogenicity is different from *RS*-stereogenicity in relevant groups to be considered:

1. *RS*-stereogenicity is defined by the convertibility due to the *RS*-permutation group $\mathbf{O}_{\bar{\imath}}$ (Eq. 15), which is contained as a subgroup in $\mathbf{S}^{[6]}$. In this meaning, the *RS*-permutation group $\mathbf{O}_{\bar{\imath}}$ is called *an RS-stereogenic group*. The *RS*-stereogenicity provides us with a basis for describing *C/A*-descriptors (or *R/S*-descriptors in organic stereochemistry, etc.) to specify absolute configurations. This has been described in terms of Def. 2.

2. Stereogenicity is defined by the convertibility due to the permutation part $\mathbf{S}^{[6]}$ (Eq. 16), which is contained in the stereoisomeric group $\mathbf{S}^{[6]}_{\mathbf{O}_{h\bar{\imath}\bar{I}}}$ (Eq. 17). In this meaning the permutation part $\mathbf{S}^{[6]}$ is called *a stereogenic group*. This has been described in terms of Def. 3. The stereogenicity provides us with a basis for describing configuration indices. The stereogenicity other than the *RS*-stereogenicity is more distinctly defined as the term *ortho-stereogenicity* (Def. 1).

Note that these concepts satisfy Eq. 19. This difference holds true in general when we consider groups other than the groups derived from $\mathbf{O}_h$.

4.1.2 Ortho-Diastereomeric Relationships and Enantiomeric Ones

Equivalence between stereoisograms **253** and **254** (Fig. 13), both of which belong to Type II, should be examined further from a view point of ortho-stereogenicity. This type of equivalence has once been discussed in case of square-planar complexes [14].

The stereoisogram **253** is converted into the stereoisogram **254** by a permutation $(3\ 5\ 4)$ $(= (3\ 4)^{-1}(4\ 5) = (3\ 4)(4\ 5))$, which contains no reflection operation. Other permutations such as $(3\ 5)$, $(2\ 4)$, etc. bring out equivalent modes of conversion. This means that the two stereoisograms are ortho-diastereomeric to each others according to Def. 1. By means of the permutation $(3\ 5\ 4)$, an enantiomeric pair of **250/$\overline{\mathbf{250}}$** (in the stereoisogram **253**) is converted into an enantiomeric pair of **251/$\overline{\mathbf{251}}$** (in the stereoisogram **254**), which is afterward identified with a pair of **$\overline{\mathbf{250}}$/250**.

These conversions are summarized to give a skew-stereoisogram shown in Fig. 14, where the word "skew" stems from quadruple-headed arrows, which denote ortho-diastereomeric relationships. They are different from *RS*-diastereomeric relationships in a (usual) stereoisogram. Although the pair of **$\overline{\mathbf{250}}$/250** has the reverse order of appearance in comparison with the pair of **250/$\overline{\mathbf{250}}$** and although the interconversion between the two pairs requires a reflection operation, each of these pairs has been preliminarily paired so that these pairs are equalized from a viewpoint of the stereoisogram approach. By following the process of recognition, we are able to say that the ortho-diastereomeric relationship coincides with the enantiomeric relationship.

The coincidence by the ortho-stereogenicity shown in Fig. 14 is seemingly akin to the coincidence in a Type I stereoisogram, which is concerned with *RS*-stereogenicity. However, the ortho-stereogenicity has nothing to do with the capability of giving *A/C*-descriptors. The capability of giving *A/C*-descriptors should be examined by means of the stereoisogram of Type II (**253** or **254**), which shows the incapability of giving *A/C*-descriptors, as shown by Eq. 70.

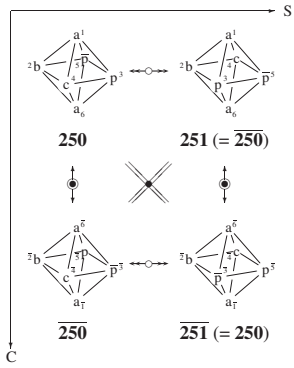


Figure 14: A skew-stereoisogram for octahedral complexes with *(OC-6-14)-* and *(OC-6-15)-*[$Ma_2bcp\overline{p}$] (cf. Eq. 70).

Note that the ortho-diastereomeric relationship between **250** and **251** (= $\overline{\mathbf{250}}$) is not a pairwise relationship. They are characterized by configuration indices, i.e., *OC-6-14* and *OC-6-15*, respectively (cf. Eq. 70), in which the two digits 14 correspond to the axes a—a (1), b—p (4), and c—$\overline{\text{p}}$ in **250**, while the two digits 15 correspond to the axes a—a (1), b—$\overline{\text{p}}$ (5), and c—p in **251** (= $\overline{\mathbf{250}}$). In contrast, the enantiomeric relationship between **250** and $\overline{\mathbf{250}}$ (= **251**) is not characterized by *(*A/C)-descriptors of IR-9.3 of the IUPAC recommendations 2005 [11]. These facts indicate that both configuration indices and *(*A/C)-descriptors do not directly specify enantiomeric relationships (nor chirality).

According to Quotation 1 of the Introduction, the center of **250** (in **253**) is "stereogenic" (due to the first sentence) and determined to be "a chiral center" (due to the second sentence) if we obey the conventional terminology. However, the "chiral center" of **250** (in **253**) is not characterized by an *A/C*-descriptor, as discussed in the preceding paragraph (cf. Eq. 70). This fact indicates that the original naming of *A/C*-descriptors as "chirality symbols" in the IUPAC recommendations 2005 [11] is inadequate. If they are called "stereogenicity symbols", it is also inadequate. They should be called *RS-stereogenicity symbols*, because such Type II cases are incapable of being determined by *A/C*-descriptors in accord with their *RS-a*stereogenicities.

In contrast, equivalence between stereoisograms **215** and **216** (Fig. 12) exhibits a different feature from the above case, although both of the stereoisograms belong to Type II. The stereoisogram **215** is converted into the stereoisogram **216** by the permutation (3 5 4), where they are coincident with each other. According to Def. 1, they are not ortho-diastereomeric. They should be referred to as being self-ortho-diastereomeric, if we restrict our consideration to the stereoisograms **215** and **216**, strictly speaking (however, note that the stereoisogram **215** (or **216**) is ortho-stereogenic if we take account of the whole of Fig. 12). By means of the permutation (3 5 4), an enantiomeric pair of **212**/$\overline{\mathbf{212}}$ (in the stereoisogram **215**) is converted into an enantiomeric pair of **213**/$\overline{\mathbf{213}}$ (in the stereoisogram **215**), which is identical to a pair of **250**/$\overline{\mathbf{250}}$ (with the same order of appearance). It follows that the self-ortho-diastereomeric relationship has nothing to do with the capability of giving *A/C*-descriptors.

4.1.3 Oversimplified Dichotomy Between Enantiomers and "Diastereomers"

The conventional stereochemistry provides us with inconsistent explanation on Type I, III, and V cases as follows:

1. (Conventional explanation on Type I cases)

   Let us apply the permutation $\tilde{\sigma}_{h(1)}$ ($\sim (1\,6)(2)(3)(4)(5)$) to **48**. This operation is regarded as producing the corresponding enantiomer $\overline{\mathbf{48}}$ in the conventional stereochemistry (compare this with Stereoisogram **54** of Fig. 3). The effect of the permutation $\tilde{\sigma}_{h(1)}$ is mixed up with the effect of the reflection $\sigma_{h(1)}$ ($\sim \overline{(1\,6)(2)(3)(4)(5)}$) so that the initial operation of $\tilde{\sigma}_{h(1)}$ is nullified to explain the total feature of the conversion. It should be noted that one enantiomeric pair (**48**/$\overline{\mathbf{48}}$) participates in this conversion from a viewpoint of the conventional stereochemistry.

2. (Conventional explanation on Type III cases)

   On the other hand, the same operation $\tilde{\sigma}_{h(1)}$ converts **257** into **258**, where **257** and **258** are "diastereomeric" in the conventional stereochemistry (compare this with Stereoisogram **262** of Fig. 13). The same operation $\tilde{\sigma}_{h(1)}$ is presumed to exhibit different effects to **48** and **257** in the conventional stereochemistry. It should be noted that two enantiomeric pairs (**257**/$\overline{\mathbf{257}}$ and **258**/$\overline{\mathbf{258}}$) participate in this conversion from a viewpoint of the conventional stereochemistry.

3. (Conventional explanation on Type V cases)

   Furthermore, the same operation $\tilde{\sigma}_{h(1)}$ converts **255** into **256**, where **255** and **256** are "diastereomeric" in the conventional stereochemistry. Note that **255** and **256** are achiral and exhibit no enantiomeric relationships. The same operation $\tilde{\sigma}_{h(1)}$ again exhibits different effects to **48** and **255** in the conventional stereochemistry (compare this with Stereoisogram **261** of Fig. 13). It should be noted that two achiral promolecules (**255** and **256**) participate in this conversion from a viewpoint of the conventional stereochemistry.

The three modes of explanation reveal the inconsistency of the conventional stereochemistry. That is to say, the permutation $\tilde{\sigma}_{h(1)}$ is correlated to a "diastereomeric" relationship in the conventional explanations for Type III and V cases, whereas the same operation $\tilde{\sigma}_{h(1)}$ is so nullified as to give preference to an "enantiomeric" relationship in the conventional explanation for Type I cases.

To justify the nullification of the permutation $\tilde{\sigma}_{h(1)}$ (as well as of the corresponding "diastereomeric" relationship) in the conventional explanation for Type I cases, the dichotomy between enantiomers and diastereomers has been proposed and widespread in the conventional stereochemistry. For example, the definition described in page 31 of [6] is as follows: "Diastereomers (or diastereoisomers) are stereoisomers (i.e., isomers of identical constitution but differing three-dimensional architecture) that do not bear a mirror-image relation to each other." Quotation 1 of the Introduction can be regarded as another version of the dichotomy because "diastereomeric" relationships stem from "stereogenicity". However, the dichotomy has only concealed the inconsistency of the three modes of explanation and has provided us with no essential solutions to the inconsistency.

In contrast, the stereoisogram approach gives a consistent explanation to cases of Type I (e.g., **48** in Stereoisogram **54** of Fig. 3), Type III (e.g., **257** in Stereoisogram **262** of Fig. 13),

and and Type V (e.g., **255** in Stereoisogram **261** of Fig. 13). The crux of the stereoisogram approach is the concept of *RS*-stereoisomers which is added as an intermediate concept between enantiomers and stereoisomers. In this paper as Part II of this series, multiplets of stereoisograms (e.g., Fig. 3) are proposed as a diagrammatic tool to comprehend the concept of *RS*-stereoisomers as an intermediate concept.

4.2 *RS*-Stereoisomerism and Stereoisomerism

On the other hand, when the stereoisomeric group $\mathbf{S}^{[6]}_{\mathbf{O}_{h\bar{i}\bar{I}}}$ (Eq. 17) operates onto a promolecule derived from the octahedral skeleton (**1**), there appears a set of stereoisomers with maintaining or changing the configurations of ligands. In other words, rotoreflection operations are involved in $\mathbf{S}^{[6]}_{\mathbf{O}_{h\bar{i}\bar{I}}}$ (Eq. 17). This convertibility due to the stereoisomeric group is referred to as *stereoisomerism*.

It should be noted that stereoisomerism is different from *RS*-stereoisomerism in relevant groups to be considered:

1. *RS*-Stereoisomerism is defined by the convertibility due to the *RS*-stereoisomeric group $\mathbf{O}_{h\bar{i}\bar{I}}$ (Eq. 1 or Eq. 2) which is contained as a subgroup in the stereoisomeric group $\mathbf{S}^{[6]}_{\mathbf{O}_{h\bar{i}\bar{I}}}$ (Eq. 17). The *RS*-stereoisomerism provides us with a basis for describing the relationship between chirality and *RS*-stereogenicity (as well as sclerality), where stereoisograms serve as a versatile tool for specifying the relationship.

2. Stereoisomerism is defined by the convertibility due to the stereoisomeric group $\mathbf{S}^{[6]}_{\mathbf{O}_{h\bar{i}\bar{I}}}$ (Eq. 17). Because the convertibility in a stereoisogram is concerned with the *RS*-stereoisomerism, the stereoisomerism is mainly concerned with the convertibility between stereoisograms, although *RS*-stereoisomerism is contained in stereoisomerism.

This difference holds true in general when we consider groups other than the groups derived from $\mathbf{O}_h$.

Because of the above-mentioned difference, the term *stereoisomerism* is regarded as an extension of the term *RS*-stereoisomerism, i.e.,

$$\begin{aligned} \text{chirality} + \textit{RS}\text{-stereogenicity} + \text{sclerality} &= \textit{RS}\text{-stereoisomerism} \\ &\subset \text{stereoisomerism.} \end{aligned} \tag{73}$$

Thus, the term *RS-stereoisomerism* characterizes features among promolecules contained in a stereoisogram, while the term *stereoisomerism* characterizes features among promolecules in the same and different stereoisograms.

It should be emphasized that we are able to discuss chirality successfully in terms of *RS*-stereoisomerism, i.e., by means of stereoisograms, as found in Eq. 73. In contrast, the conventional stereochemistry lacks the concept of *RS*-stereoisomerism based on the concept of stereoisogram, so that chirality has been discussed in terms of stereoisomerism, which has provided confused situations described in the Introduction.

4.3 Paradigm Shift for Equivalence Classes

The stereoisogram approach reveals that we are able to discuss chirality in terms of stereoisograms, which contain enantiomeric relationships (for discussing chirality), *RS*-diastereomeric

relationships (for discussing *RS*-stereogenicity), and holantimeric relationships (for discussing sclerality). The discussion of chirality requires *RS*-stereogenicity as a counterpart concept for the purpose of consistent discussion, as discussed in Part I of this series. As discussed in the present article as Part II of this series, the discussion of chirality does not require stereogenicity (or ortho-stereogenicity, more specifically speaking), so that Quotation 1 and Quotation 2 are concluded to be misleading so as to cause the confusing situations of the conventional stereochemistry, which have been pointed out in the Introduction.

From a viewpoint of equivalence classes, the methodology of the conventional stereochemistry stems from a scheme shown in Fig 15(a), where enantiomeric relationships are used to describe equivalence classes, while diastereomeric relationships have no effects, especially in Type I cases. When the relationship denoted by the symbol (*) stems from the operation of $\tilde{\sigma}_{h(1)}$ ($\sim$ (1 6)(2)(3)(4)(5)) on a Type I case (e.g., Stereoisogram **54** of Fig. 3), either one of the two equivalence classes linked with an underbrace is neglected because of the preference of enantiomeric relationships over diastereomeric ones. As a result, the remaining equivalence class is regarded as being operated by $\sigma_{h(1)}$ (in place of $\tilde{\sigma}_{h(1)}$) so as to generate a pair of enantiomers as an equivalence class. In other words, the relationship denoted by the symbol (*) is neglected in Type I cases.

More precisely speaking, the word "neglected" in the conventional stereochemistry means that a single equivalence class for describing a Type I case is presumed from the beginning instead of considering degeneration of the two equivalence classes linked by an underbrace. This treatment of a Type 1 case is biased in comparison with a Type III or IV case without considering such degeneration even in the conventional stereochemistry. In other words, an equivalence class of Type I is different from an equivalence class of Type III or V in the scheme shown in Fig 15(a). These features have been overlooked in the conventional stereochemistry.

To remedy such confusing situations, Def. 3 is given as the revised definition of the term *diastereomeric* (and *stereogenic*) in place of the conventional definition (e.g., Quotation 1) of the term "diastereomeric" (and "stereogenic"). Note that the newly-defined term *stereogenic* is expected to be used in combination with *RS*-stereogenicity, so that the relationship denoted by the symbol (*) is not neglected even in Type I cases.

The revisions provided by the stereoisogram approach are based on a kind of conceptional restriction in which the concept of *RS*-stereogenicity is separated definitely and meaningfully from the concept of stereogenicity. The restricted concept *RS-stereogenicity* is linked with an *RS-diastereomeric relationship* as a pairwise relationship. Note that a "diastereomeric" relationship linked with the concept of "stereogenicity" is not a pairwise relationship. The pairwise feature of the *RS*-diastereomeric relationship is correlated to an enantiomeric relationship as a pairwise relationship derived from the concept of chirality. Then, these concepts are integrated into the concept of *RS-stereoisomerism*, which is represented diagrammatically by a stereoisogram composed of a quadruplet of promolecules (cf. Part I of this series).

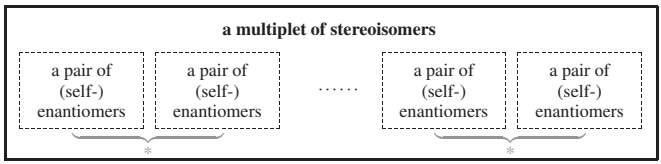
This kind of conceptional restriction (or the creation of an intermediate concept from a reverse point of view) has been important in chemistry. For example, Avogadro clarified that the concept of *molecule* should be added between *gas* and *atom* to rationalize Gay-Lussac's law of combining volumes of gases [15, page 119–123].

In the context of organic and inorganic stereochemistry, the hierarchy of such concepts is summarized schematically as follows:

$$\text{atoms} \rightarrow \text{molecules} \rightarrow \text{enantiomers} \rightarrow \text{stereoisomers},$$

where a name list for the establishment of relevant fields contains Pasteur [16, 17], van't Hoff

(a) Equivalence classes under enantiomeric relationships



(b) Equivalence classes under *RS*-stereoisomeric relationships

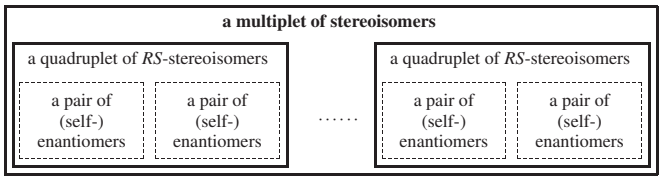


Figure 15: A paradigm shift for equivalence classes. (a) Equivalence classes under enantiomeric relationship without describing the relationship * in the conventions of stereochemistry. (b) Equivalence classes under *RS*-stereoisomeric relationships in the present approach [9].

[18, 19], Le Bel [20], Fischer [21, 22], Werner [23, 24], and others. By means of the stereoisogram approach [1–3], the concept of *RS*-stereoisomers is added between enantiomers and stereoisomers, so as to generate a new hierarchy as follows (cf. Eq. 73):

$$\text{atoms} \rightarrow \text{molecules} \rightarrow \text{enantiomers} \rightarrow \textit{RS}\text{-stereoisomers} \rightarrow \text{stereoisomers}. \tag{}$$

The stereoisogram approach provides us with a reliable basis shown in Fig 15(b), where quadruplets of *RS*-stereoisomers are considered to be equivalence classes. Such quadruplets are degenerated or not degenerated in accord with the corresponding stereoisograms of Type I–V. Typical examples are found in Figs. 3–5, 12, and 13. The schemes in Fig 15(a) and (b), which have originally been reported for organic stereochemistry [9], are also effective to inorganic stereochemistry. Thus, the paradigm shift from Fig 15(a) to Fig 15(b) is inevitable in organic and inorganic stereochemistry.

5 Conclusions

Stereogenic groups and stereoisomeric groups are defined by starting from *RS*-stereoisomeric groups for characterizing stereoisograms and the symmetric group of degree 6. Multiplets of stereoisograms are defined on the basis of the stereoisomeric groups. Thereby, the difference between *RS*-stereogenicity and stereogenicity as well as between *RS*-stereoisomerism and stereoisomerism is determined decisively after group-theoretical consideration. The stereoisogram approach, which has originally been developed to rationalize organic stereochemistry [1, 9, 25], is clarified to be effective to inorganic stereochemistry. Stereogenicity has nothing to do with the capability of giving *C*/*A*-descriptors, which is, in turn, ascribed to *RS*-stereogenicity (or *RS*-diastereomeric relationships), but not to chirality. Both the concept of stereogenicity and the concept of *RS*-stereogenicity are independent to the concept of chirality, although the *RS*-stereogenicity interacts with chirality.

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