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Point Groups, *RS*-Stereoisomeric Groups, Stereoisomeric Groups, and Isoskeletal Groups for Characterizing Square-Planar Complexes. Hierarchy of Groups for Restructuring Stereochemistry (Part 2)

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Abstract

The hierarchy of groups for square-planar complexes is determined to be: point groups = *RS*-stereoisomeric groups ⊂ stereoisomeric groups = isoskeletal groups. The *RS*-nomenclature is not effective to name square-planar complexes, because the *RS*-stereoisomeric groups coincide with the point groups so that all square-planar complexes are determined to be *RS*-astereogenic. There exist no isoskeletal isomers for square-planar complexes, because the isoskeletal groups coincide with the stereoisomeric groups. To discuss the stereogenicity, we propose the concept of *extended stereoisogram*, which contains three degenerate stereoisograms. Thereby, square planar-complexes are classified into Types II-II-II, IV-IV-IV, etc. on the basis of relevant stereoisograms (Types I to V). The number 3 of the degenerate stereoisograms in an extended stereoisogram means that square-planar complexes cannot be named by a dichoromus nomenclature such as the *RS*-nomenclature and the *E*/*Z*-nomenclature.

1 Introduction

It has been believed that chirality gives a basis of discussing stereochemistry, whereas stereogenicity gives a basis of discussing stereochemical nomenclature. However, the entangled relationship between chirality and stereogenicity has frequently provided organic chemists and biochemists with confusion, as pointed out by several reviews [1, 2]. The confusion has mainly stemed from the lack of a common mathematical basis to discuss chiraly and stereogenicity in a balanced fashion. Although chirality (or stereochemistry) is ascribed to geometrical consideration by point-group theory, stereogenicity (or stereochemical nomenclature) has no mathematical tool to be relied on.

The purpose of this series is to obtain a ballaced and systematic overview on stereochemistry as well as on stereochemical nomenclature, where the hierarchy of groups exhibits various features according to the geometrical nature and the nomenclature nature of skeletons (e.g., allene, ethylene, and others). Thus, in the previous paper of this series (Part 1), we have described a common mathematical basis for discussing the stereochemistry and the stereochemical nomenclature of allene derivatives [3].

With respect to derivatives of ligancy 4, tetrahedral and allene derivatives have been named by the *RS*-nomenclature [4], ethylene derivatives by the *E*/*Z*-nomenclature [5, 6], and square-planar complexes by the other inorganic nomenclature (polyhedron descriptors) [7, 8]. What does this difference stem from? The bases of the *RS*-nomenclature for teterahedral molecules [9, 10] and for allene derivatives [3] have been discussed by means of a new terminology for groups (point groups, *RS*-permutation groups, *RS*-stereoisomeric groups, stereoisomeric groups, and isoskeletal groups) as well as a new terminology for isomers (enantiomers, holantimers, *RS*-diastereomers, and isoskeletal isomers). Thereby, as for tetrahedral molecules [9, 10] and allene derivatives [3], a common feature has been demonstrated as follows: *RS*-stereoisomeric groups coincide with stereoisomeric groups.

One of the remaining tasks is to examine whether or not this approach is effective to square-planar complexes of ligancy 4. To accomplish this task, we should examine square-planar complexes as a general case in which *RS*-stereoisomeric groups do not coincide with stereoisomeric groups. The results of square-planar complexes will be applied to rationalize the fact that their configurations are characterized by the inorganic nomenclature (the polyhedron descriptors) [7, 8].

2 Groups for Characterizing a Square-Planar Skeleton

Figure 1 shows the groups that act on the four positions of a squar-planar skeleton.

1. The point group D_{4h} of order 16 is considered to discuss the geometrical aspect (chirality) of square-planar complexes. More precisely speaking, the coset representation $\mathrm{D}_{4h}(/\mathrm{C}''_{2v})$ is used to describe the four positions of a square-planar skeleton, where the degree of each permutation is calculated to be $|\mathrm{D}_{4h}|/|\mathrm{C}''_{2v}| = 16/4 = 4$ [11]. This coset representation is regarded as a permutation representation, where permutations corresponding to improper rotations (rotoreflections) are designated by overbars. The permutations of $\mathrm{D}_{4h}(/\mathrm{C}''_{2v})$ for proper rotations coincide with the permutations for improper rotations if the designation by an overbar is omitted.

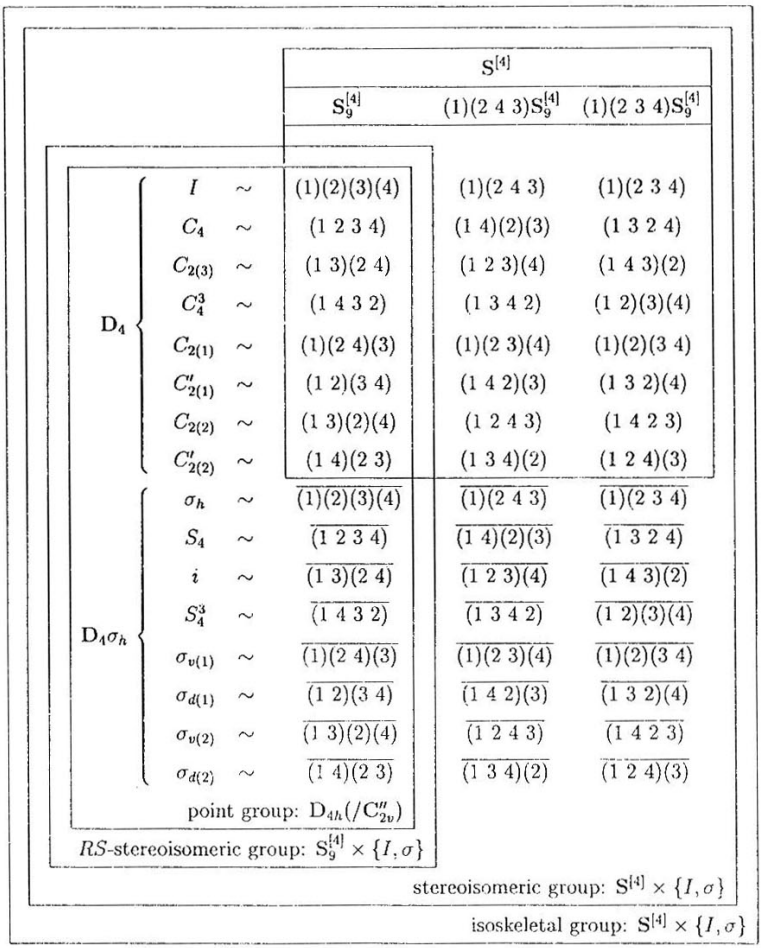

Figure 1: Point group, *RS*-stereoisomeric group, stereomeric group, and isoskeletal group for square-planar complexes.

We also refer to the coset representation $\mathbf{D}_{4h}(/\mathbf{C}''_{2v})$ as the group $\mathbf{D}_{4h}$, if such usage causes no confusion.

2. The group for characterizing the *RS*-stereogenicity of square-planar complexes can be represented by a direct product $\mathbf{S}_9^{[4]} \times \{I, \sigma\}$ ($\sigma = \sigma_h$), where the group $\mathbf{S}_9^{[4]}$ is a subgroup of the symmetric group of degree 4 (i.e., $\mathbf{S}^{[4]}$). Note that the operation σ can be selected from rotoreflections. We can use $\sigma = \sigma_h$, which is contained in the group $\mathbf{D}_{4h}$. The group $\mathbf{S}_9^{[4]} \times \{I, \sigma\}$ coincides with the group $\mathbf{D}_{4h}$ so that each stereoisogram based on the square-planar skeleton inherently belongs to Type II [9]. It follows that that square-planar complexes are *RS*-astereogenic so as not to be named by *RS*-descriptors.

3. To discuss the nomenclature aspect (stereogenicity) of square-planar complexes, we should discriminate *RS*-(a)stereogenicity from usual-defined stereogenicity. For this purpose, we consider the symmetric group of degree 4 (i.e., $\mathbf{S}^{[4]}$), where we obtain the coset decomposition:

$$\mathbf{S}^{[4]} = \mathbf{S}_9^{[4]} + (1)(2\ 4\ 3)\mathbf{S}_9^{[4]} + (1)(2\ 3\ 4)\mathbf{S}_9^{[4]} \tag{1}$$

Obviously, this group characterizes the stereoisomerism (usual stereogenicity) of square-planar complexes. However, we use the term "*m*-stereogenicity" to designated the stereoisomerism (*m*: "meta" of Greek origin), because the present usage is slightly different from the traditional term "stereogenicity", which corresponds to the present terms "*RS*-stereogenicity" and "*m*-stereogenicity".

4. To integrate the two aspects (chirality and stereogenicity), we define the stereoisomeric group of the square-planar skeleton as a direct product represented by $\mathbf{S}^{[4]} \times \{I, \sigma\}$. This group contains the symmetric group $\mathbf{S}^{[4]}$ as a normal subgroup.

5. We have already considered the action of the symmetric group $\mathbf{S}^{[4]}$ on the four positions of the square-planar skeleton, as described above. Hence, we cannot obtain constitutional isomers (isoskeletal isomers). In other words, the stereoisomeric group coincides with the isoskeletal group, as shown in Fig. 1.

According to the group-subgroup relationship shown in Fig. 1, the isomerism of square-planar complexes is represented by the following hierarchy: isoskeletal isomers ($\mathbf{S}^{[4]} \times \{I, \sigma\}$) = stereoisomers ($\mathbf{S}^{[4]} \times \{I, \sigma\}$) $\supset$ *RS*-stereoisomers ($\mathbf{S}_9^{[4]} \times \{I, \sigma\}$) = enantiomers ($\mathbf{D}_{4h}$). In accord with a ligand pattern, the group-subgroup relationship varies within this hierarchy.

3 Extended Stereoisograms

A square-planar molecule having ligands ABCp is taken as an example for showing the action of the isoskeletal group $\mathbf{S}^{[4]} \times \{I, \sigma\}$.

3.1 *RS*-Stereoisomeric Groups and Degenerate Stereoisograms

The concepts of holantimer and stereoisogram proposed by the author [9] are applied to square-planar complexes (Fig. 2). The *RS*-stereoisomeric group for a square-planar

skelton is identical with the point group, as shown in Fig. 1. It follows that the holantimer of a square-planar complex (e.g., $\bar{1}$b) of an original molecule (e.g., **1a**) is always identical with the corresponding enantiomer (e.g., $\bar{1}$a) and that the *RS*-diastereomer (e.g., **1b**) is identical with the original molecule (e.g., **1a**), as shown in the left stereoisogram of Fig. 2. As a result, the stereoisogram of each square-planar complex needs not contain the holantimer and the *RS*-diastereomer so that the S-axis of the stereoisogram is degenerate, as shown in the right degenerate stereoisogram of Fig. 2.

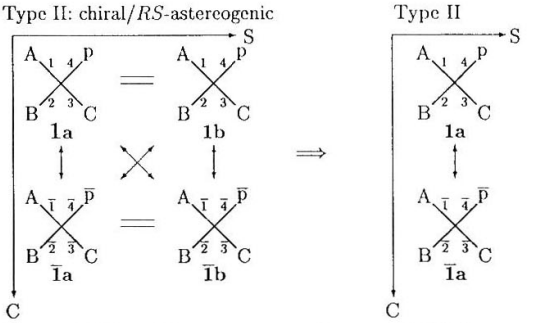

Figure 2: Stereoisogram (left) and degenerate stereoisogram (right) for a squar-planar complex with ligands ABCp (or ABC$\bar{\text{p}}$). They are concerned with the *RS*-stereoisomeric group $S_9^{[4]} \times \{I, \sigma\}$.

Degenerate stereoisograms such as Fig. 2 correspond to the *RS*-astereogenic nature of the square-planar skeleton (Type II or Type IV) so that square-planar complexes are not characterized by the *RS*-nomemclature. The concept of holantimers would be unnecessary if we start directly from the hierarchy shown in Fig. 1. However, the concept defined on a non-mathematical basis is useful to test the *RS*-stereogenicity or *RS*-astereogenicity of a given skeleton.

3.2 Stereoisomeric Groups and Extended Stereoisograms

The exhaustive enumeration of square-planar complexes has been reported by using the point group $\mathbf{D}_{4h}$ and the symmetric group $\mathbf{S}^{[4]}$ separately in a previous paper, which did not take account of the *RS*-stereoisomeric group and the concept of stereoisogram [12]. The concept of stereoisogram provides us with the concept of *extended stereoisogram*, which is useful to discuss the stereoisomerism of square-planar complexes.

3.3 Extended Stereoisograms of Type II-II-II

The action of the stereoisomeric group $\mathbf{S}^{[4]} \times \{I, \sigma\}$ generates six parts according to the following cosets: $\mathbf{S}_9^{[4]}$ and $\overline{(1)(2)(3)(4)}\mathbf{S}_9^{[4]}$; $(1)(2\ 4\ 3)\mathbf{S}_9^{[4]}$ and $\overline{(1)(2\ 4\ 3)}\mathbf{S}_9^{[4]}$; and $(1)(2\ 3\ 4)\mathbf{S}_9^{[4]}$ and $\overline{(1)(2\ 3\ 4)}\mathbf{S}_9^{[4]}$, where the transversal is represented by

$$\{(1)(2)(3)(4), \overline{(1)(2)(3)(4)}; (1)(2\ 4\ 3), \overline{(1)(2\ 4\ 3)}; (1)(2\ 3\ 4), \overline{(1)(2\ 3\ 4)}\}. \qquad (2)$$

Each of the six parts contains a set of homomers, from which a representative is selected on the basis of the transversal shown in eq. 2. Thus, the numbering of the original molecule **1a** is permuted according to the transversal (eq. 2) so as to place ligands in accord with the function: $f(1)$ = A, $f(2)$ = B, $f(3)$ = C, $f(4)$ = p. Thereby, we obtain molecules collected in Fig. 3. The diagram shown in Fig. 3 is called *extended stereoisogram*. Since this extended stereoisogram consists of three degenerate stereoisograms of Type II, it is designated by the symbol II-II-II, where the separation with hyphens indicates that the relevant stereoisograms are concerned with a single stereoisomeric group.

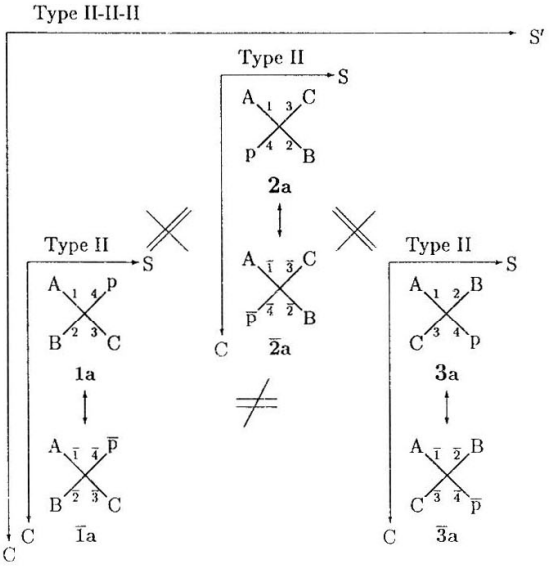

Figure 3: Extended stereoisogram (II-II-II) for a squar-planar complex with ligands ABCp (or ABC$\bar{\text{p}}$). They are concerned with the stereoisomeric group $\mathbf{S}^{[4]} \times \{I, \sigma\}$.

If the priority of the ligands is presumed to be A > B > C > p, the complex **1a** is determined to be SP-4-3, the complex **2a** is determined to be SP-4-2, and the complex **3a** is determined to be SP-4-4.

Extended stereoisograms (II-II-II) similar to Fig. 3 are found for ligand patterns such as ABCp, ABpq, Ap$\bar{\text{p}}$q, Apqr, p$\bar{\text{p}}$qr, and pqrs.

3.4 Extended Stereoisograms of Type IV-IV-IV

Figure 4 shows a set of three degenerate stereoisograms for ligands ABCD under the setereoiomeric group $\mathbf{S}^{[4]} \times \{I, \sigma\}$. By using the same numbering as listed above, the ligands are placed in accord with the function: $f(1)$ = A, $f(2)$ = B, $f(3)$ = C, $f(4)$

= D. Thereby, representative molecules (Fig. 4) generate an extended stereoisogram, which contains three degenerate stereoisograms of Type IV (achiral/*RS*-astereogenic). These degenerate stereoisograms are different from each other. This type of extended stereoisogram is designated by the symbol IV-IV-IV.

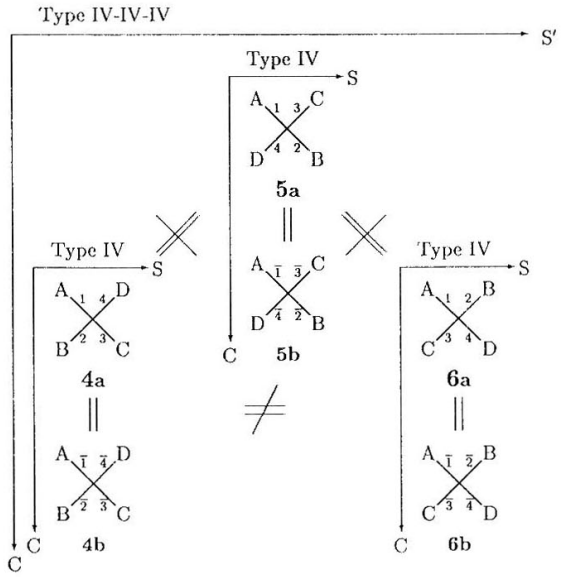

Figure 4: Extended stereoisogram (Type IV-IV-IV) for a squar-planar complex with ligands ABCD. They are concerned with the stereoisomeric group $S^{[4]} \times \{I, \sigma\}$.

If the priority of the ligands is presumed to be A > B > C > D, the complex **4a** is determined to be *SP*-4-3, the complex **5a** is determined to be *SP*-4-2, and the complex **6a** is determined to be *SP*-4-4.

Extended stereoisograms (IV-IV-IV) similar to Fig. 4 are found for ligand patterns such as ABCD and $p\bar{p}q\bar{q}$.

3.5 Extended Setereoisograms of Type II^2-II

Figure 5 shows an extended stereoisogram for ligands A^2p^2 under the stereoisomeric group $S^{[4]} \times \{I, \sigma\}$. The ligands are placed in accord with the function: $f(1)$ = A, $f(2)$ = p, $f(3)$ = A, $f(4)$ = p. By collecting representative molecules, the extended stereoisogram (Fig. 5) is obtained. It consists of three degenerate stereoisograms of Type II, two of which are identical with each other and different from the remaining one. Hence, this extended stereoisogram is designated by the symbol II^2-II.

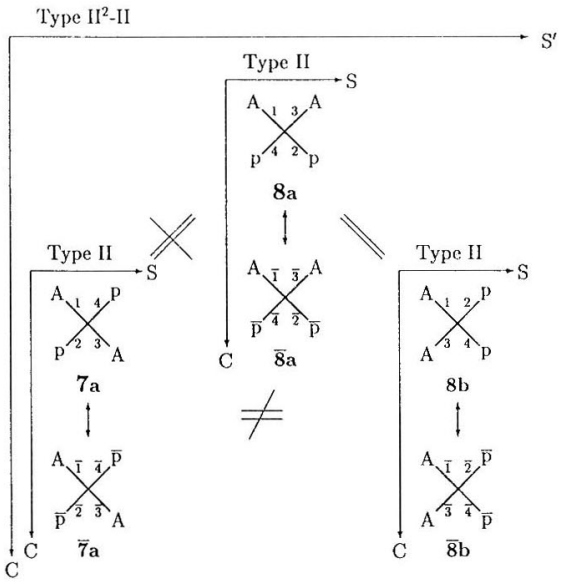

Figure 5: Extended stereoisogram (Type II²-II) for a squar-planar complex with ligands A^2p^2. They are concerned with the stereoisomeric group $S^{[4]} \times \{I, \sigma\}$.

If the priority of the ligands is presumed to be A > p, the complex **7a** is determined to be *SP*-4-1 and the complex **8a** (= **8b**) is determined to be *SP*-4-2.

Extended stereoisograms (II²-II) similar to Fig. 5 are found for ligand patterns such as A^2p^2, A^2Bp, A^2pq, ABp^2, p^2q^2, $Ap^2\bar{p}$, Ap^2q, $p^2\bar{p}q$, $p^2q\bar{q}$, and p^2qr.

3.6 Extended Setereoisograms of Type IV²-IV

Figure 6 shows an extended stereoisogram for ligands A^2B^2 under the stereoisomeic group $S^{[4]} \times \{I, \sigma\}$. The function, $f(1) = A$, $f(2) = A$, $f(3) = B$, $f(4) = B$, is applied to generate an extended stereoisogram (Fig. 6), which contains three degenerate stereoisograms. The two of them are identical with each other and different from the remaining one. Hence, it is characterized as Type IV²-IV.

If the priority of the ligands is presumed to be A > B, the complex **9a** is determined to be *SP*-4-1 and the complex **10a** (= **10c**) is determined to be *SP*-4-2.

Extended stereoisograms (IV²-IV) similar to Fig. 6 are found for ligand patterns such as A^2B^2, $p^2\bar{p}^2$, A^2BC, and $A^2p\bar{p}$.

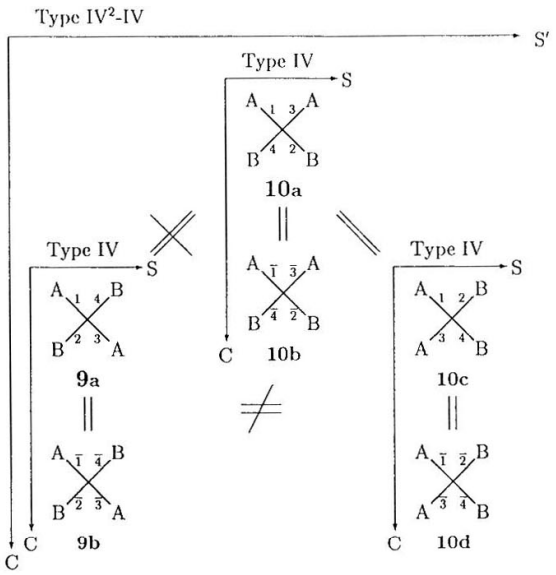

Figure 6: Extended stereoisogram (Type IV²-IV) for a squar-planar complex with ligands A^2B^2. They are concerned with the stereoisomeric group $S^{[4]} \times \{I, \sigma\}$.

3.7 Extended Setereoisograms of Type II³

Figure 7 shows an extended stereoisogram for ligands A^3p under the stereoisomeric group $S^{[4]} \times \{I, \sigma\}$. The ligands are placed in accord with the function: $f(1) = A$, $f(2) = A$, $f(3) = A$, $f(4) = p$. Thereby, we obtain representative molecules collected in Fig. 7.

The three degenerate stereoisograms contained in the entended stereoisogram are identical with one another and belong to Type II. Hence, the extended stereoisogram is designated by the symbol II^3.

Even if the priority of the ligands is presumed to be A > p, there exists only one stereoisomer so that its configuration specification for *SP*-4 is unnecessary.

Extended stereoisograms (II^3) similar to Fig. 7 are found for ligand patterns such as p^4, A^3p, Ap^3, $p^3\bar{p}$, and p^3q.

3.8 Extended Setereoisograms of Type IV³

Figure 8 shows an extended stereoisogram for ligands A^3B under the stereoisomeric group $S^{[4]} \times \{I, \sigma\}$. We place ligands in accord with the function: $f(1) = A$, $f(2) = A$, $f(3) = A$, $f(4) = B$. Thereby, representative molecules are generated, as collected in Fig. 8.

The three degenerate stereoisograms contained in the extended stereoisogram are identical with one another and belong to Type IV. Hence, the extended stereoisogram is

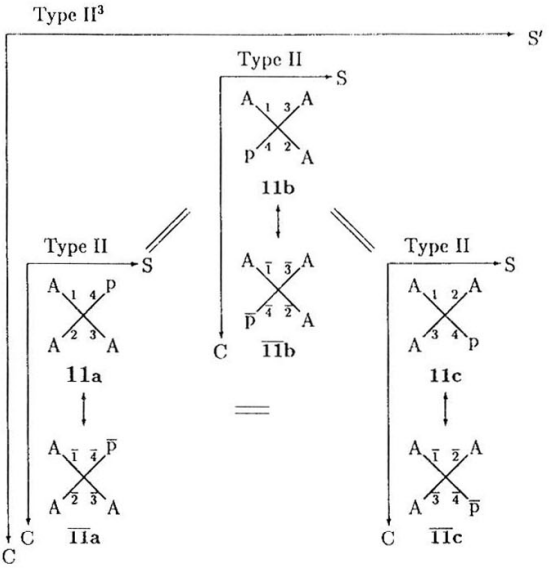

Figure 7: Extended stereoisogram (Type II³) for a squar-planar complex with ligands A³p. They are concerned with the stereoisomeric group $\mathbf{S}^{[4]} \times \{I, \sigma\}$.

designated by the symbol IV³.

Even if the priority of the ligands is presumed to be A > B, there exists only one stereoisomer so that its configuration specification for *SP*-4 is unnecessary. The ligand patterns A³B and A⁴ are obtained as examples of extended stereoisograms (IV³).

3.9 Extended Setereoisograms of Type II=II-IV

Figure 9 shows a special extended stereoisogram for ligands ABp$\overline{\text{p}}$ under the stereoisomeric group $\mathbf{S}^{[4]} \times \{I, \sigma\}$. The ligands ABp$\overline{\text{p}}$ are placed in accord with the function: $f(1)$ = A, $f(2)$ = B, $f(3)$ = p, $f(4)$ = $\overline{\text{p}}$. Thereby, three degenerate stereoisograms are obtained to construct an extended stereoisogram of Type II=II-IV, where the ligand pattern ABp$\overline{\text{p}}$ is a sole example. We adopt the symbol II=II-IV in place of II²-IV, because **13a** shown in the first stereoisogram of Fig. 9 is converted into $\overline{\textbf{13b}}$ shown in the third stereoisogram of Fig. 9. Note that they are enantiomeric to each other.

The adoption of the symbol II=II-IV in place of II²-IV is rationalized by the naming of the complexes. If the priority of the ligands is presumed to be A > B > p > $\overline{\text{p}}$, the complex **13a** is determined to be *SP*-4-3 and the complex **14a** is determined to be *SP*-4-2. Moreover, the complex $\overline{\textbf{13b}}$, should be named *SP*-4-4, although the complex $\overline{\textbf{13b}}$, is identical with $\overline{\textbf{13a}}$ which is enantiomeric to the complex **13a**.

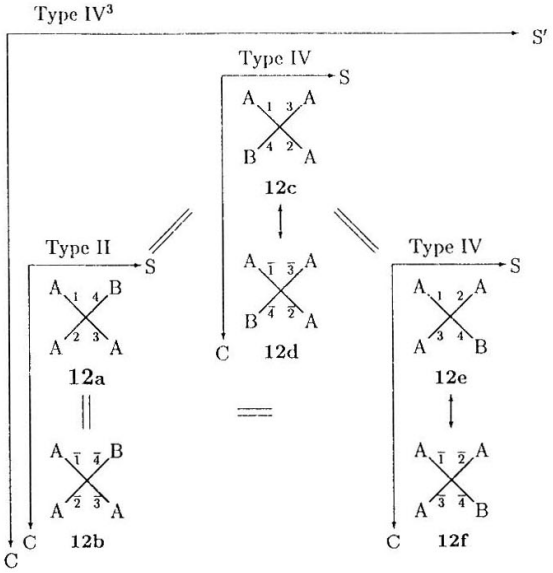

Figure 8: Extended stereoisogram (Type IV^3) for a squar-planar complex with ligands A^{3}B. They are concerned with the stereoisomeric group $S^{[4]} \times \{I, \sigma\}$.

3.10 Polyhedron Descriptors for Square-Planar Complexes

Table 1 shows a list of square-planar complexes with various ligand patterns, where the symbol Y indicates the presence of a polyhedron descriptor and the symbol N indicates the absence of a polyhedron descriptor.

The stereochemical nomenclature is based on the *RS*-stereogenicity (S-axis) and the *m*-stereogenicity (S′-axis). The *RS*-stereogenicity (S-axis) [3, 9] has been proved to provide a foundation for the *RS*-nomenclature [4]. On the other hand, the *m*-stereogenicity (S′-axis) has been proved in this article to require the system of polyhedron descriptors for square-planar complexes [7, 8], where dichotomy is impossible according to the nature of the extended stereoisogram containing three stereoisograms. On the other hand, the *E*/*Z*-nomenclature [5, 6] is also based on *m*-stereogenicity, where the dichotomy *E*/*Z* has been proved to be possible according to the nature of the extended stereoisogram containing two stereoisograms. This point will be discussed in detail in future.

4 Conclusions

The hierarchy of point groups, *RS*-stereoisomeric groups, and stereoisomeric groups is discussed to comprehend the chirality, *RS*-stereogenicity, and *m*-stereogenicity for square-

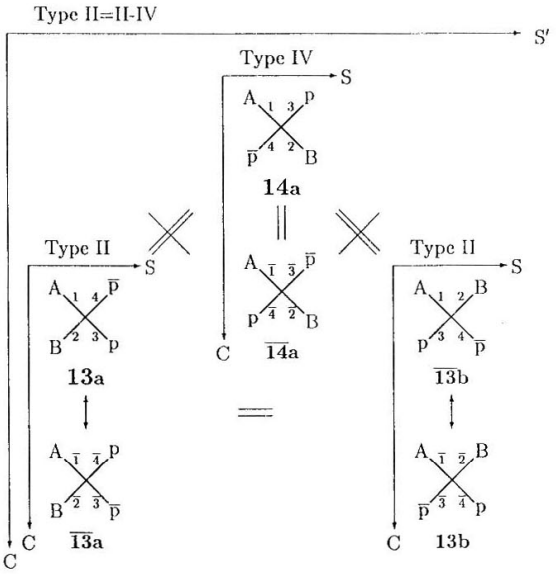

Figure 9: Extended stereoisogram (Type II=II-IV) for a squar-planar complex with ligands ABp$\overline{\text{p}}$. They are concerned with the stereoisomeric group $S^{[4]} \times \{I, \sigma\}$.

Table 1: Extended Stereoisograms for Square-Planar Complexes

Type		polyhedron descriptor	example (ligand pattern)
IV-IV-IV	(Fig. 4)	Y-Y-Y	ABCD, p$\overline{\text{p}}$q$\overline{\text{q}}$
II^2-II	(Fig. 5)	Y-Y	A^{2}p^2, A^{2}Bp, A^{2}pq, ABp^2, p^{2}q^2, Ap$^2\overline{\text{p}}$, Ap^{2}q, p$^2\overline{\text{p}}$q, p^{2}q$\overline{\text{q}}$, p^{2}qr
II^3	(Fig. 7)	none	p^4, A^{3}p, Ap^3, p$^3\overline{\text{p}}$, p^{3}q
II-II-II	(Fig. 3)	Y-Y-Y	ABCp, ABpq, Ap$\overline{\text{p}}$q, Apqr, p$\overline{\text{p}}$qr, pqrs
IV^2-IV	(Fig. 6)	Y-Y	A^{2}B^2, p$^2\overline{\text{p}}^2$, A^{2}BC, A^{2}p$\overline{\text{p}}$
IV^3	(Fig. 8)	none	A^{3}B, A^4
II=II-IV	(Fig. 9)	Y=Y-Y	ABp$\overline{\text{p}}$

planar complexes. Since the *RS*-stereoisomeric groups coincide with the point groups (i.e., *RS*-astereogenic), the *RS*-nomenclature is not effective to name square-planar complexes. Since the isoskeletal groups coincide with the stereoisomeric groups, there exist no isoskeletal isomers for square-planar complexes. To discuss the *m*-stereogenicity, we have proposed the concept of *extended stereoisogram*, which contains three degenerate stereoisograms. Thereby, square planar-complexes are classified into Types II-II-II, IV-IV-IV, etc. on the basis of relevant stereoisograms (Types I to V).

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