

Chirality and Stereogenicity of Square-Planar Complexes

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Square-planar complexes with achiral and chiral ligands have been enumerated exhaustively under the point-group D_{4h} and under the symmetry group S^4 of degree 4, where they have been classified in terms of their symmetries and permutabilities. Thereby, their stereochemical properties and relationships have been discussed in detail. In particular, equivalency under point-group symmetry (*e.g.*, enantiomeric relationships for chiral complexes and prochirality for achiral complexes) and that under permutation-group symmetry (*e.g.*, proper and improper permutations, stereogenic and astereogenic groups, and enantioselective and diastereogenic groups) have been characterized to give a systematic format for stereochemistry and stereoisomerism.

1. Introduction. – Although configuration of organic and inorganic molecules have been investigated by numerous methodologies, there exists a common theoretical standpoint in which they are based on polyhedral and polygonal models; *e.g.*, a tetrahedral model proposed by *van't Hoff* for configuration of organic molecules [1] and octahedral and square-planar models proposed by *Werner* for configuration of inorganic molecules [2]. Thus, vast experimental results have been accumulated and explained from the standpoint, as summarized in textbooks on organic [3] and inorganic stereochemistry [4]. Unfortunately, however, the standpoint has been implemented in two ways for organic as well as for inorganic stereochemistry.

The first way is a practical and experimental one that has been adopted in most textbooks on organic and inorganic stereochemistry [3][4], where distinct models are discussed specifically and rather separately. For example, both the tetrahedral molecule **1** and the square-planar molecule **2** belong to the same C_{2v} symmetry, whereas they have different geometric arrangements (*Fig. 1*). As long as we rely on the first way, we have only a qualitative method for distinguishing them. Moreover, the first way does not provide us with a systematic methodology in reasoning that the tetrahedral molecule (**1**) has no diastereoisomer, while the square-planar molecule **2** has a diastereoisomer (**3**).

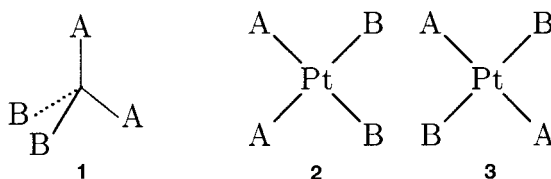


Fig. 1. Molecules of ligancy 4

The second way is based on a mathematical framework that was founded by the pioneering work published in this journal [5], where a group-theoretical and combinatorial approach provides us with general and quantitative methods for covering all such models [6–8]. This way should be pursued further, since putting a theory into an abstract mathematical format is an ultimate target of science. However, the generality of the theory should always be ascertained with practical scientific problems to make the mathematical format of the theory acceptable to both experimental and theoretical chemists.

As a methodology of the second way, we have pointed out the importance of coset representations $\mathbf{G}/(\mathbf{G}_i)$ to give a systematic format to organic and inorganic configurations. We have then proposed the concept of sphericity on the basis of the chirality/achirality properties of the groups \mathbf{G} and \mathbf{G}_i [9], which has been applied to the redefinition of prochirality [9][10], topicity [8][11], stereogenicity [11], and anisochrony [12]. We have further proposed the subduction of coset representations as a new concept [13] and have applied it to combinatorial enumeration [13], to the classification of molecular symmetries [14], and to the design of achiral and chiral molecules [15]. Although our approach has been applied to inorganic compounds such as octahedral complexes [16] and ferrocene derivatives [17], our efforts have mainly focused on organic stereochemistry [18][19].

The present paper deals with the stereochemistry of square-planar complexes as typical model for inorganic stereochemistry, where the ligancy-4 character of a square-planar skeleton (such as **2** and **3**) will be compared with that of a tetrahedral skeleton (such as **1**). The present discussion on the \mathbf{D}_{4h} symmetry of the square-planar skeleton, which has several subgroups in common with the \mathbf{T}_d symmetry of the tetrahedral-skeleton for organic stereochemistry, will reveal essential features of inorganic stereochemistry. Moreover, the comparison between the point group \mathbf{D}_{4h} and the symmetry group of degree 4 ($\mathbf{S}^{[4]}$) will provide us with a deeper insight into the chirality and stereogenicity of square-planar complexes.

2. Symmetry of Square-Planar Complexes. – 2.1. *Mark Table for \mathbf{D}_{4h} .* The square-planar skeleton **4** (Fig. 2), in which the symbol A represents an achiral ligand and the symbol M represents a metal, belongs to the point group \mathbf{D}_{4h} [20]. This point group involves 16 symmetry operations as follows:

$$\mathbf{D}_{4h} = \{I, C_4, C_{2(3)}, C_4^3, C_{2(1)}, C'_{2(1)}, C_{2(2)}, C'_{2(2)}; \sigma_h, S_4, i, S_4^3, \sigma_{v(1)}, \sigma_{d(1)}, \sigma_{v(2)}, \sigma_{d(2)}\} \quad (1)$$

The operation $C_{2(3)}$ is a rotation by 180° around a four-fold axis perpendicular to the square-planar skeleton. The four-fold axis accompanies rotations C_4 and C_4^3 , which generate rotoreflections S_4 and S_4^3 by virtue of σ_h . Note that the operation σ_h is a reflection with respect to the plane of the square. Each of the operations $C_{2(1)}$ and $C_{2(2)}$ is a dihedral rotation by 180° around a two-fold axis through the linear arrangement of the bonds A–M–A. The operations $C'_{2(1)}$ and $C'_{2(2)}$ are another set of dihedral rotations by 180° around two-fold axes, each of which bisects the angle between the adjacent bonds A–M–A. The operation i is an inversion with respect to the center. The

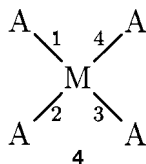


Fig. 2. Numbering of a square-planar skeleton

operations $\sigma_{v(1)}$ and $\sigma_{v(2)}$ are reflections due to mirror planes, each of which is perpendicular to the plane of the complex and contains the bonds A–M–A. The operations $\sigma_{d(1)}$ and $\sigma_{d(2)}$ are reflections due to mirror planes bisecting the adjacent angle A–M–A.

The point group \mathbf{D}_{4h} has 27 subgroups up to conjugacy. When two or more groups belong to the same point group but are not conjugate within \mathbf{D}_{4h} , they are differentiated by adding primes. For example, the point groups \mathbf{C}_2 , \mathbf{C}'_2 , and \mathbf{C}''_2 represent chiral subgroups of order 2, which represent $\mathbf{C}_2 = \{I, C_{2(3)}\}$, $\mathbf{C}'_2 = \{I, C_{2(1)}\}$, and $\mathbf{C}''_2 = \{I, C_{2(2)}\}$, respectively. The respective two-fold axes correspond to those of \mathbf{C}_{2h} , \mathbf{C}'_{2h} , and \mathbf{C}''_{2h} . The two-fold axis for the point group \mathbf{C}_2 is in common with \mathbf{C}_{2v} and \mathbf{C}'_{2v} . On the other hand, the two-fold axis for \mathbf{C}'_2 corresponds to \mathbf{C}''_{2v} , while that for \mathbf{C}''_2 corresponds to \mathbf{C}_{2v} .

The four positions of the square-planar skeleton are equivalent and are, therefore, an orbit (equivalence class). By application of a general procedure described in [8], the orbit is determined to be governed by a coset representation (CR) $\mathbf{D}_{4h}/(\mathbf{C}''_{2v})$.

For the purpose of accomplishing this assignment and for the subsequent combinatorial enumeration, we use a mark table for \mathbf{D}_{4h} (Fig. 3), which is calculated from the multiplication table of \mathbf{D}_{4h} . We regard the mark table (Fig. 3) as a 27 by 27 matrix (M), where the row or column number (27) is equal to the number of inequivalent subgroups. Thereby, we can obtain its inverse (M^{-1}), which is also useful for combinatorial enumeration. When the four positions are numbered from 1 to 4 as shown in Fig. 2, a permutation representation is obtained as follows:

$$\begin{aligned} \mathbf{D}_{4h}/(\mathbf{C}''_{2v}) = \{ & (1)(2)(3)(4), (1234), (13)(24), (1432), \\ & (1)(24)(3), (12)(34), (13)(2)(4), (14)(23), \\ & \overline{(1)(2)(3)(4)}, \overline{(1234)}, \overline{(13)(24)}, \overline{(1432)}, \\ & \overline{(1)(24)(3)}, \overline{(12)(34)}, \overline{(13)(2)(4)}, \overline{(14)(23)} \} \end{aligned} \quad (2)$$

where the permutations on the right-hand side correspond to the elements of Eqn. 1 in this order. Each permutation with an overline represents an improper rotation of \mathbf{D}_{4h} , which produces a mirror image. By starting from the permutation representation (Eqn. 2), we obtain a fixed-point vector (FPV) as follows:

$$\text{FPV} = (4,0,2,0,2,0,4,0,0,0,0,2,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0) \quad (3)$$

where we count fixed points when restricted into each subgroup. Since the FPV is equal to the $\mathbf{D}_{4h}/(\mathbf{C}''_{2v})$ row of the mark table shown in Fig. 3, the permutation representation

four A's¹) to give the complex **4** shown in *Fig. 2*, while a molecule (*e.g.*, **2** or **3**) belonging to a subsymmetry is obtained by putting an appropriate set of different ligands (*e.g.*, A²B²)²). The derivation process of **2**, for example, is represented by a subduction of the CR $\mathbf{D}_{4h}/(\mathbf{C}_{2v}'')$ into the subgroup \mathbf{C}_{2v}''' . The subgroup $\mathbf{C}_{2v}''' (= \{i, C_{2(1)}, \sigma_h, \sigma_{d(1)}\})$ is assigned to a permutation representation:

$$\mathbf{D}_{2h}/(\mathbf{C}_s'') \downarrow \mathbf{C}_{2v}''' = \{(1)(2)(3)(4), (12)(34), \overline{(1)(2)(3)(4)}, \overline{(12)(34)}\} \quad (5)$$

Thereby, the four positions are divided into two sets (orbits) of positions, {1, 2} and {3, 4}. Since these orbits are respectively governed by $\mathbf{C}_{2v}'''/(\mathbf{C}_s')$, they accommodate A² and B² separately. This process is represented by the following equation:

$$\mathbf{D}_{2h}/(\mathbf{C}_s'') \downarrow \mathbf{C}_{2v}''' = 2\mathbf{C}_{2v}'''/(\mathbf{C}_s') \quad (6)$$

Such a sum of CRs as appearing on the right-hand side can be precalculated algebraically with respect to each subgroup with mark tables and inverse mark tables for \mathbf{D}_{4h} and the subgroup \mathbf{G}_i . Although this procedure has been shown for general cases in our book [8], the subduction concerning \mathbf{D}_{4h} has not been reported because the mark table and its inverse for \mathbf{D}_{4h} have not been reported. The present results for the $\mathbf{D}_{4h}/(\mathbf{C}_s')$ orbit are collected in *Table 1*.

Each sum of CRs collected in *Table 1* represents a ligand partition to produce a square-planar derivative, where each CR corresponds to an orbit of ligands and is characterized by its sphericity (enantiospheric, homospheric, and hemispheric) [8][9]. Since the sphericity is concisely represented by a dummy variable (*i.e.*, a_d for a homospheric orbit, b_d for a hemispheric orbit, or c_d for an enantiospheric orbit), each sum of CRs is represented by a product of such dummy variables, where the subscript d represents the size of the orbit at issue. The product of dummy variables is called a unit subduced cycle index with chirality fittingness (USCI-CF), which is listed in *Table 1* [8][9]. When the sphericities are ignored by substituting a dummy variable s_d for a_d , b_d , and c_d , a unit subduced cycle index (USCI) without chirality fittingness is obtained, as listed also in *Table 1*.

3. Combinatorial Enumeration of Square-Planar Complexes. – 3.1. *Enumeration under Point-Group Symmetry.* We have reported four methods of the USCI approach for combinatorial enumeration [21][22]. Among them, we here use the PCI method [23] (the generating-function method based on partial cycle indices (PCIs)) including an extension for taking account of chirality fittingness. The USCI-CFs listed in *Table 1* are aligned and regarded as a hypothetical row vector, which is multiplied by the matrix of the inverse mark table (M^{-1}) for \mathbf{D}_{4h} . This treatment can be symbolically represented by the following expression:

$$\begin{aligned} & (b_1^4, b_2^2, b_1^2 b_2, b_2^2, a_1^2 c_2, c_2^2, a_1^4, c_2^2, b_4, c_4, a_2^2, c_4, a_1^2 a_2, a_2^2, a_2^2, \\ & a_2 c_2, c_4, b_2^2, b_4, a_4, a_4, c_4, a_4, a_2^2, a_4, b_4, a_4) \times M^{-1} \end{aligned} \quad (7)$$

²) A term A²B² is used in place of A₂B₂ for the consistency with the combinatorial enumeration described in this article.

Table 1. Subductions of $\mathbf{D}_{4h}(\mathbf{C}_{2v})^a$

Subduction	USCI-CF	Eqn. No.
$\mathbf{D}_{4h}(\mathbf{C}_{2v}) \downarrow \mathbf{C}_1 = 4\mathbf{C}_1(\mathbf{C}_1)$	b_1^4	34
$\mathbf{D}_{4h}(\mathbf{C}_{2v}) \downarrow \mathbf{C}_2 = 2\mathbf{C}_1(\mathbf{C}_1)$	b_2^2	35
$\mathbf{D}_{4h}(\mathbf{C}_{2v}) \downarrow \mathbf{C}_2 = \mathbf{C}_3(\mathbf{C}_1) + 2\mathbf{C}_2(\mathbf{C}_2)$	$b_1^2 b_2$	36
$\mathbf{D}_{4h}(\mathbf{C}_{2v}) \downarrow \mathbf{C}_2'' = 2\mathbf{C}_2(\mathbf{C}_1)$	b_2^2	37
$\mathbf{D}_{4h}(\mathbf{C}_{2v}) \downarrow \mathbf{C}_s = \mathbf{C}_s(\mathbf{C}_1) + 2\mathbf{C}_s(\mathbf{C}_s)$	$a_1^2 c_2$	38
$\mathbf{D}_{4h}(\mathbf{C}_{2v}) \downarrow \mathbf{C}_s' = 2\mathbf{C}_s(\mathbf{C}_1)$	c_2^2	39
$\mathbf{D}_{4h}(\mathbf{C}_{2v}) \downarrow \mathbf{C}_s'' = 4\mathbf{C}_s(\mathbf{C}_s)$	a_1^4	40
$\mathbf{D}_{4h}(\mathbf{C}_{2v}) \downarrow \mathbf{C}_i = 2\mathbf{C}_i(\mathbf{C}_1)$	c_2^2	41
$\mathbf{D}_{4h}(\mathbf{C}_{2v}) \downarrow \mathbf{C}_4 = \mathbf{C}_4(\mathbf{C}_1)$	b_4	42
$\mathbf{D}_{4h}(\mathbf{C}_{2v}) \downarrow \mathbf{S}_4 = \mathbf{S}_4(\mathbf{C}_1)$	c_4	43
$\mathbf{D}_{4h}(\mathbf{C}_{2v}) \downarrow \mathbf{C}_{2v} = \mathbf{C}_{1v}(\mathbf{C}_s) + \mathbf{C}_{2v}(\mathbf{C}_s)$	a_2^2	44
$\mathbf{D}_{4h}(\mathbf{C}_{2v}) \downarrow \mathbf{C}_{2v}' = \mathbf{C}_{2v}(\mathbf{C}_1)$	c_4	45
$\mathbf{D}_{4h}(\mathbf{C}_{2v}) \downarrow \mathbf{C}_{2v}'' = \mathbf{C}_{2v}(\mathbf{C}_s) + 2\mathbf{C}_{2v}(\mathbf{C}_{2v})$	$a_1^2 a_2$	46
$\mathbf{D}_{4h}(\mathbf{C}_{2v}) \downarrow \mathbf{C}_{2v}''' = 2\mathbf{C}_{2v}(\mathbf{C}_s)$	a_2^2	47
$\mathbf{D}_{4h}(\mathbf{C}_{2v}) \downarrow \mathbf{C}_{2h} = 2\mathbf{C}_{2h}(\mathbf{C}_s)$	a_2^2	48
$\mathbf{D}_{4h}(\mathbf{C}_{2v}) \downarrow \mathbf{C}_{2h}' = \mathbf{C}_{2h}(\mathbf{C}_2) + \mathbf{C}_{2h}(\mathbf{C}_s)$	$a_2 c_2$	49
$\mathbf{D}_{4h}(\mathbf{C}_{2v}) \downarrow \mathbf{C}_{2h}'' = \mathbf{C}_{2h}(\mathbf{C}_1)$	c_4	50
$\mathbf{D}_{4h}(\mathbf{C}_{2v}) \downarrow \mathbf{D}_2 = \mathbf{D}_2(\mathbf{C}_2) + \mathbf{D}_2(\mathbf{C}_s)$	b_2^2	51
$\mathbf{D}_{4h}(\mathbf{C}_{2v}) \downarrow \mathbf{D}_2' = \mathbf{D}_2(\mathbf{C}_1)$	b_4	52
$\mathbf{D}_{4h}(\mathbf{C}_{2v}) \downarrow \mathbf{C}_{4v} = \mathbf{C}_{4v}(\mathbf{C}_s)$	a_4	53
$\mathbf{D}_{4h}(\mathbf{C}_{2v}) \downarrow \mathbf{C}_{4h} = \mathbf{C}_{4h}(\mathbf{C}_s)$	a_4	54
$\mathbf{D}_{4h}(\mathbf{C}_{2v}) \downarrow \mathbf{D}_{2d} = \mathbf{D}_{2d}(\mathbf{C}_2)$	c_4	55
$\mathbf{D}_{4h}(\mathbf{C}_{2v}) \downarrow \mathbf{D}_{2d}' = \mathbf{D}_{2d}(\mathbf{C}_s)$	a_4	56
$\mathbf{D}_{4h}(\mathbf{C}_{2v}) \downarrow \mathbf{D}_{2h} = \mathbf{D}_{2h}(\mathbf{C}_{2v}) + \mathbf{D}_{2h}(\mathbf{C}_s)$	a_2^2	57
$\mathbf{D}_{4h}(\mathbf{C}_{2v}) \downarrow \mathbf{D}_{2h}' = \mathbf{D}_{2h}(\mathbf{C}_s)$	a_4	58
$\mathbf{D}_{4h}(\mathbf{C}_{2v}) \downarrow \mathbf{D}_4 = \mathbf{D}_4(\mathbf{C}_2)$	b_4	59
$\mathbf{D}_{4h}(\mathbf{C}_{2v}) \downarrow \mathbf{D}_{4h} = \mathbf{D}_{4h}(\mathbf{C}_{2v})$	a_4	60

^{a)} For the meaning of symbols, see text.

Thereby, we obtain the partial cycle index with chirality fittingness (PCI-CF) for every subgroup:

$$\begin{aligned} \text{PCI-CF}(\mathbf{C}_1, \$_d) &= \frac{1}{16} b_1^4 - \frac{1}{16} b_2^2 - \frac{1}{8} b_1^2 b_2 - \frac{1}{8} a_1^2 c_2 - \frac{3}{16} c_2^2 - \frac{1}{16} a_1^4 \\ &\quad + \frac{1}{8} b_4 + \frac{3}{8} c_4 + \frac{1}{4} a_1^2 a_2 + \frac{1}{4} a_2 c_2 - \frac{1}{2} a_4 \end{aligned} \quad (8)$$

$$\text{PCI-CF}(\mathbf{C}_2, \$_d) = \frac{1}{4} b_1^2 b_2 - \frac{1}{4} a_1^2 a_2 - \frac{1}{4} a_2 c_2 - \frac{1}{4} b_2^2 + \frac{1}{2} a_2^2 \quad (9)$$

$$\text{PCI-CF}(\mathbf{C}_2'', \$_d) = \frac{1}{4} b_2^2 - \frac{1}{4} a_2^2 - \frac{1}{4} c_4 - \frac{1}{4} b_4 + \frac{1}{4} a_4 \quad (10)$$

$$\text{PCI-CF}(\mathbf{C}_s, \$_d) = \frac{1}{4} a_1^2 c_2 + \frac{1}{4} a_2^2 - \frac{1}{4} a_1^2 a_2 - \frac{1}{4} a_4 c_2 \quad (11)$$

$$\text{PCI-CF}(\mathbf{C}_s', \$_d) = \frac{1}{4} c_2^2 - \frac{1}{2} c_4 - \frac{1}{4} a_2^2 + \frac{1}{2} a_4 \quad (12)$$

$$\text{PCI-CF}(\mathbf{C}'_s, \$_d) = \frac{1}{8}a_1^4 - \frac{1}{4}a_1^2a_2 - \frac{1}{8}a_2^2 + \frac{1}{4}a_4 \quad (13)$$

$$\text{PCI-CF}(\mathbf{C}_i, \$_d) = \frac{1}{8}c_2^2 + \frac{1}{8}a_2^2 - \frac{1}{4}a_2c_2 - \frac{1}{4}c_4 + \frac{1}{4}a_4 \quad (14)$$

$$\text{PCI-CF}(\mathbf{C}'_{2v}, \$_d) = \frac{1}{2}a_1^2a_2 - \frac{1}{2}a_2^2 \quad (15)$$

$$\text{PCI-CF}(\mathbf{C}''_{2v}, \$_d) = \frac{1}{2}a_2^2 - \frac{1}{2}a_4 \quad (16)$$

$$\text{PCI-CF}(\mathbf{C}'_{2h}, \$_d) = \frac{1}{2}a_2c_2 - \frac{1}{2}a_2^2 \quad (17)$$

$$\text{PCI-CF}(\mathbf{C}''_{2h}, \$_d) = \frac{1}{2}c_4 - \frac{1}{2}a_4 \quad (18)$$

$$\text{PCI-CF}(\mathbf{D}_2, \$_d) = \frac{1}{4}b_2^2 - \frac{1}{4}c_4 - \frac{1}{4}a_2^2 - \frac{1}{4}b_4 + \frac{1}{2}a_4 \quad (19)$$

$$\text{PCI-CF}(\mathbf{D}_{2d}, \$_d) = \frac{1}{2}c_4 - \frac{1}{2}a_4 \quad (20)$$

$$\text{PCI-CF}(\mathbf{D}_{2h}, \$_d) = \frac{1}{2}a_2^2 - \frac{1}{4}a_4 \quad (21)$$

$$\text{PCI-CF}(\mathbf{S}_4, \$_d) = \frac{1}{2}b_4 - \frac{1}{2}a_4 \quad (22)$$

$$\text{PCI-CF}(\mathbf{D}_{4h}, \$_d) = a_4 \quad (23)$$

where the symbol $\$_d$ represents a set of a_d , b_d , and c_d for the sake of simplicity. Since the PCI-CFs for \mathbf{C}_2 , \mathbf{C}_4 , \mathbf{S}_4 , \mathbf{C}_{2v} , \mathbf{C}'_{2v} , \mathbf{C}_{2h} , \mathbf{D}'_2 , \mathbf{C}_{4v} , \mathbf{C}_{4h} , \mathbf{D}'_{2d} , and \mathbf{D}'_{2h} vanish, they are omitted in this list of PCI-CFs. It should be emphasized that the disappearance of a PCI-CF represents the nonexistence of complexes belonging to the corresponding point group within the scope of the definition of USCI-CFs¹). In fact, if a ligand A belongs to a supergroup of \mathbf{C}_{2v} or, if a proligand A is taken into consideration [20], the resulting A^4 complex undergoes no symmetry restriction, exhibiting \mathbf{D}_{4h} symmetry in agreement with the CR $\mathbf{D}_{4h}(\mathbf{C}'_{2v})$. In other words, possible complexes having \mathbf{C}_{4v} , \mathbf{C}_{4h} , \mathbf{D}'_{2d} , and \mathbf{D}'_{2h} coalesce to give the \mathbf{D}_{4h} complex.

The discussion described in the preceding paragraph can be qualitatively explained by comparing the USCI-CFs collected in *Table 1*, where the procedure described in [14] for judging the existence of subsymmetries is applied to the present cases. For example, the subductions into \mathbf{C}_{4v} , \mathbf{C}_{4h} , \mathbf{D}'_{2d} , and \mathbf{D}'_{2h} correspond to the same USCI-CF (a_4), which is identical to that of \mathbf{D}_{4h} . Hence, they are grouped into \mathbf{D}_{4h} , as long as ligand symmetries do not disturb the local symmetry of the $\mathbf{D}_{4h}(\mathbf{C}'_{2v})$ orbit. On the other hand, the subductions into \mathbf{C}_4 , \mathbf{D}'_2 , and \mathbf{D}_4 correspond to the same USCI-CF (b_4) but different from that (a_4) of \mathbf{D}_{4h} . Hence, complexes of the possible symmetries coalesce to give a

\mathbf{D}_4 complex. Similarly, the complexes of \mathbf{C}_{2v} , \mathbf{C}_{2h} , and \mathbf{D}_{2h} are grouped to give \mathbf{D}_{2h} complexes because of the same USCI-CF (a_2^2). Although \mathbf{C}_{2v}'' corresponds to the same USCI-CF (a_2^2), the \mathbf{C}_{2v}''' complex can exist because \mathbf{C}_{2v}''' is not a subgroup of \mathbf{D}_{2h} . The symmetries \mathbf{S}_4 , \mathbf{C}_{2v}' , and \mathbf{D}_{2d} are grouped into \mathbf{D}_{2d} , because the subduction data show the same USCI-CF (c_4), which is different from that (a_4) of \mathbf{D}_{4h} . In spite of the same USCI-CF (c_4), a \mathbf{C}_{2h}'' complex is available, because \mathbf{C}_{2h}'' is not a subgroup of \mathbf{D}_{2d} .

When we directly rely on the subductions collected in *Table 1*, we are able to discuss cases in which ligand symmetries mismatch the local symmetry of the $\mathbf{D}_{4h}(\mathbf{C}_{2v}'')$ orbit [20]. For example, if a ligand has the symmetry \mathbf{C}_s that is lower than the local symmetry \mathbf{C}_{2v}'' , it restricts the global symmetry \mathbf{D}_{4h} into either one of \mathbf{C}_{4v} , \mathbf{C}_{4h} , \mathbf{D}_{2d}' , and \mathbf{D}_{2h}' . Thus, derivatives of these subgroups can be accessible, because the subduction data collected in *Table 1* indicate that the local symmetry is \mathbf{C}_s (and related ones).

According to the three kinds of dummy variables, we use three kinds of ligand inventories as follows:

$$a_d = A^d + B^d + C^d + D^d \quad (24)$$

$$b_d = A^d + B^d + C^d + D^d + p^d + \bar{p}^d + q^d + \bar{q}^d + r^d + \bar{r}^d + s^d + \bar{s}^d \quad (25)$$

$$c_d = A^d + B^d + C^d + D^d + 2p^{d/2}\bar{p}^{d/2} + 2q^{d/2}\bar{q}^{d/2} + 2r^{d/2}\bar{r}^{d/2} + 2s^{d/2}\bar{s}^{d/2} \quad (26)$$

which are introduced into the PCI-CFs (*Eqns. 8–23*). The resulting equations are expanded to give generating functions for respective subgroups. Several examples of the generating functions are shown as follows:

$$\begin{aligned} f_{c_1} = & \left[\frac{1}{2}(A^2Bp + A^2B\bar{p}) + \frac{1}{2}(AB^2p + AB^2\bar{p}) + \dots \right] \\ & + \left[\frac{1}{2}(A^2pq + A^2\bar{p}\bar{q}) + \frac{1}{2}(B^2pq + B^2\bar{p}\bar{q}) + \dots \right] \\ & + \left[\frac{3}{2}(ABCp + ABC\bar{p}) + \frac{3}{2}(ABDp + ABD\bar{p}) + \dots \right] \end{aligned} \quad (27)$$

$$\begin{aligned} & + \left[\frac{1}{2}(ABp^2 + AB\bar{p}^2) + \frac{1}{2}(ABq^2 + AB\bar{p}^2) + \dots \right] \\ & + [ABp\bar{p} + ABq\bar{q} + \dots] + \dots \end{aligned} \quad (28)$$

$$\begin{aligned} f_{c_2} = & \left[\frac{1}{2}(A^2p^2 + A^2\bar{p}^2) + \frac{1}{2}(B^2p^2 + B^2\bar{p}^2) + \dots \right] \\ & + \left[\frac{1}{2}(p^2q^2 + \bar{p}^2\bar{q}^2) + \frac{1}{2}(p^2r^2 + \bar{p}^2\bar{r}^2) + \dots \right] \end{aligned} \quad (29)$$

$$f_{c_3} = [A^2p\bar{p} + B^2p\bar{p} + \dots] + [2p\bar{p}q\bar{q} + 2p\bar{p}r\bar{r} + \dots] \quad (30)$$

A pair of enantiomers is counted with a combined term such as $(1/2)(A^2Bp + A^2B\bar{p})$. On the other hand, the term $ABp\bar{p}$ designates a pair of enantiomers, since it is regarded

as $(1/2)(ABp\bar{p} + AB\bar{p}p)$. The resulting coefficients are listed in *Table 2*, where an arbitrary term is selected as a representative for the terms of ligand partitions of the same type that are contained in each pair of brackets of a generating function such as in *Eqns. 28–30*.

Table 2. Number of Square-Planar Complexes under \mathbf{D}_{4h} ^{a)}

	\mathbf{C}_1	\mathbf{C}_2'	\mathbf{C}_2''	\mathbf{C}_s	\mathbf{C}_s'	\mathbf{C}_s''	\mathbf{C}_i	\mathbf{C}_{2v}'	\mathbf{C}_{2v}''	\mathbf{C}_{2h}'	\mathbf{C}_{2h}''	\mathbf{D}_2	\mathbf{D}_{2d}	\mathbf{D}_{2h}	\mathbf{D}_4	\mathbf{D}_{4h}
A^4	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1
A^3B	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0
$A^3\bar{p}$	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0
A^2B^2	0	0	0	0	0	0	0	0	1	0	0	0	0	1	0	0
A^2BC	0	0	0	0	0	1	0	1	0	0	0	0	0	0	0	0
$A^2B\bar{p}$	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0
A^2p^2	0	0	1	0	0	0	0	0	0	0	0	1	0	0	0	0
$A^2p\bar{p}$	0	0	0	0	1	0	0	0	0	1	0	0	0	0	0	0
A^2pq	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0
$ABCD$	0	0	0	0	0	3	0	0	0	0	0	0	0	0	0	0
$ABC\bar{p}$	3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
ABp^2	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0
$ABp\bar{p}$	1	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0
$ABpq$	3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Ap^3	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0
$Ap^2\bar{p}$	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Ap^2q	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0
$Ap\bar{p}q$	3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
$Apqr$	3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

^{a)} Square-planar complexes of the subgroups \mathbf{C}_2 , \mathbf{C}_4 , \mathbf{S}_4 , \mathbf{C}_{2v} , \mathbf{C}_{2v}' , \mathbf{C}_{2h} , \mathbf{D}_2 , \mathbf{C}_{4v} , \mathbf{C}_{4h} , \mathbf{D}_{2d} , and \mathbf{D}_{2h} do not exist under the conditions of the present article.

The data listed in *Table 2* and additional data are illustrated in *Figs. 4* and *5*, where derivatives of the same type are depicted by an appropriate representative. As for a chiral derivative, an appropriate enantiomer is depicted as a representative.

3.2. *Enumeration under Permutation-Group Symmetry.* By the inspection of the permutations listed in *Eqn. 2*, we find that the permutations corresponding to the proper rotations (*i.e.*, \mathbf{D}_4) are the same as those for the improper rotations, if we ignore the overlines. Note that the \mathbf{D}_4 part of the CR $\mathbf{D}_{4h}/(\mathbf{C}_{2v}'')$ is equalized to the permutation group $\mathbf{S}_9^{[4]}$, which is a subgroup of the symmetric group of degree 4 ($\mathbf{S}^{[4]}$). To recognize diastereoisomerism (*e.g.*, between **2** and **3**) properly, we should add the permutations (14)(2)(3) and (12)(3)(4) (or (1)(243) and (1)(234)) to those of $\mathbf{S}_9^{[4]}$ ($\sim \mathbf{D}_4$). Thereby, we obtain the symmetric group $\mathbf{S}^{[4]}$ (order 24). The coset decomposition of $\mathbf{S}^{[4]}$ by $\mathbf{S}_9^{[4]}$ is represented by the following equation:

$$\mathbf{S}^{[4]} = \mathbf{S}_9^{[4]} + (1)(243)\mathbf{S}_9^{[4]} + (1)(234)\mathbf{S}_9^{[4]} \quad (31)$$

On an abstract level, the symmetric group $\mathbf{S}^{[4]}$ is identical to the group for a tetrahedral model (\mathbf{T}_d) [24]. Hence, we can obtain the PCIs for this case, which are found to be equal to *Eqns. 21–31* reported in [24]. Since we now take no account of chirality fittingness, we use a single type of ligand inventory as follows:

D_{4h}	D_4	D_{2h}	D_{2d}	D_2			
 5 $S_7^{[4]}$	 6 $S_7^{[4]}$	 7 $S_7^{[4]}$	 8* $S_7^{[4]}$	 9 $S_7^{[4]}$	 10 $S_7^{[4]}$		
C_{2h}''	C_{2h}'	C_{2v}'''	C_{2v}''		C_i		
 11* $S_7^{[4]}$	 12* $S_3^{[4]}$	 13 $S_7^{[4]}$	 14 $S_8^{[4]}$	 15 $S_3^{[4]}$	 16* $S_1^{[4]}$		
C_s''			C_s'		C_s		
 17 $S_3^{[4]}$	 18 $S_1^{[4]}$	 19 $S_1^{[4]}$	 20 $S_1^{[4]}$	 21* $S_3^{[4]}$	 22* $S_1^{[4]}$	 23* $S_1^{[4]}$	
 24* $S_1^{[4]}$							
C_2''		C_2'					
 25 $S_7^{[4]}$	 26 $S_7^{[4]}$	 27 $S_8^{[4]}$	 28 $S_3^{[4]}$	 29 $S_3^{[4]}$	 30 $S_3^{[4]}$	 31 $S_8^{[4]}$	 32 $S_3^{[4]}$
		 33 $S_3^{[4]}$	 34 $S_8^{[4]}$	 35 $S_8^{[4]}$	 36 $S_3^{[4]}$	 37 $S_3^{[4]}$	 38 $S_3^{[4]}$

Fig. 4. Derivation of square-planar complexes (Part I). A complex with an asterisked number is prochiral.

$$s_d = A^d + B^d + C^d + D^d + p^d + \bar{p}^d + q^d + \bar{q}^d + rd + \bar{r}^d + s^d + \bar{s}^d \quad (32)$$

where the variable s_d on the left-hand side and the s^d on the right-hand side have different meanings. The inventory (Eqn. 32) is introduced into the PCIs (Eqns. 21–31 reported in [24]), and the resulting equations are expanded to give generating functions

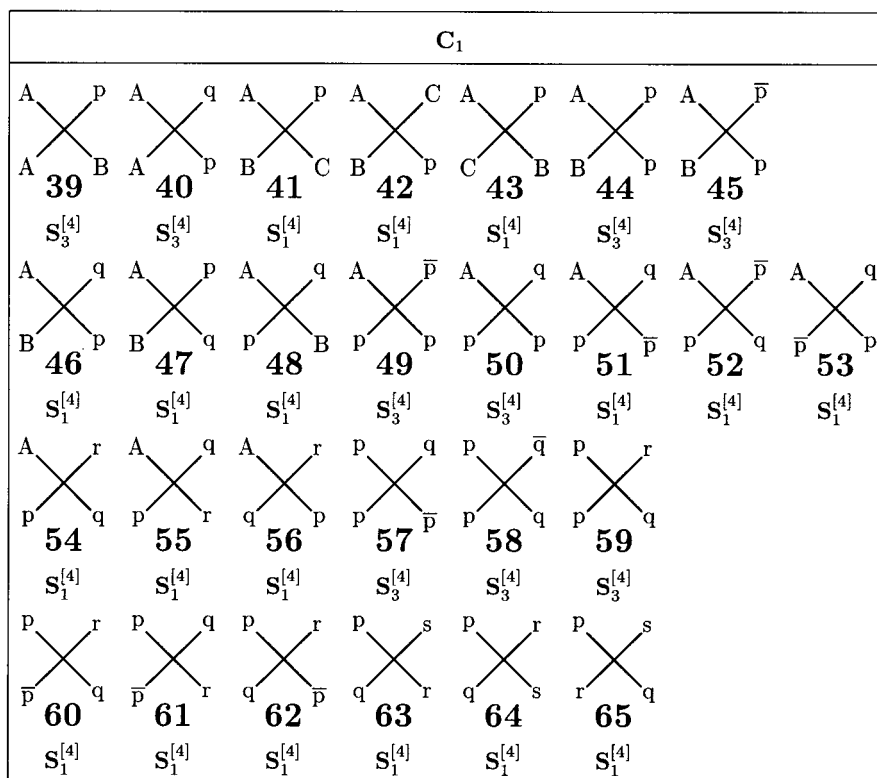


Fig. 5. Derivation of square-planar complexes (Part II)

for respective subgroups. The coefficients of the generating functions are listed in Table 3. The assignments to permutation-symmetries of square-planar complexes are added to the data listed in Figs. 4 and 5.

4. Equivalency under Point-Group Symmetry. – 4.1. *Achiral Complexes.* Let us consider equivalency under point-group symmetry by using achiral molecules of the ligand partition A^2B^2 . Table 2 shows that there are two isomers for the ligand partition A^2B^2 , which belong to D_{2h} and C_{2v} . They are depicted in Fig. 4: **7** (D_{2h}) and **13** (C_{2v}). Since they are based on a square-planar skeleton of D_{4h} symmetry, their isomer equivalency is examined on the action of the point group D_{4h} . For example, **7** is converted to sixteen homomers under D_{4h} , as shown in Fig. 6. Note that, in each derivative, the positions 1 and 3 accommodate an achiral ligand A, while the positions 2 and 4 accommodate another achiral ligand B. Since the ligands A and B are achiral, the positions $\bar{1}$ and $\bar{3}$ accommodate the ligand A, and the positions $\bar{2}$ and $\bar{4}$ accommodate the ligand B. Among the operations D_{4h} (Eqn. 1), Fig. 6 shows that the operations corresponding to D_{2h} ($=\{I, C_{2(3)}, C_{2(1)}, C_{2(2)}, C_4, \sigma_h, i, \sigma_{v(1)}, \sigma_{v(2)}\}$) keep **7** invariant. As a result, the sixteen homomers are divided into two sets of homomers, i.e., $\{7a, 7c, 7e, 7g; \bar{7}a, \bar{7}c, \bar{7}e, \bar{7}g\}$ and $\{7b, 7d, 7f, 7h; \bar{7}b, \bar{7}d, \bar{7}f, \bar{7}h\}$. These two sets construct a homospheric

Table 3. Number of Square-Planar Complexes under $S^{[4]}$

	Number of molecules										
	$S_1^{[4]}$	$S_2^{[4]}$	$S_3^{[4]}$	$S_4^{[4]}$	$S_5^{[4]}$	$S_6^{[4]}$	$S_7^{[4]}$	$S_8^{[4]}$	$S_9^{[4]}$	$S_{10}^{[4]}$	$S^{[4]}$
A^4	0	0	0	0	0	0	0	0	0	0	1
A^3B	0	0	0	0	0	0	0	1	0	0	0
A^3p	0	0	0	0	0	0	0	1	0	0	0
A^2B^2	0	0	0	0	0	0	1	0	0	0	0
A^2BC	0	0	1	0	0	0	0	0	0	0	0
A^2Bp	0	0	1	0	0	0	0	0	0	0	0
A^2p^2	0	0	0	0	0	0	1	0	0	0	0
$A^2p\bar{p}$	0	0	1	0	0	0	0	0	0	0	0
A^2pq	0	0	1	0	0	0	0	0	0	0	0
$ABCD$	1	0	0	0	0	0	0	0	0	0	0
$ABCp$	1	0	0	0	0	0	0	0	0	0	0
ABp^2	0	0	1	0	0	0	0	0	0	0	0
$ABp\bar{p}$	1	0	0	0	0	0	0	0	0	0	0
$ABpq$	1	0	0	0	0	0	0	0	0	0	0
Ap^3	0	0	0	0	0	0	0	1	0	0	0
$Ap^2\bar{p}$	0	0	1	0	0	0	0	0	0	0	0
Ap^2q	0	0	1	0	0	0	0	0	0	0	0
$App\bar{q}$	1	0	0	0	0	0	0	0	0	0	0
$Apqr$	1	0	0	0	0	0	0	0	0	0	0

orbit governed by the CR $D_{4h}/(D_{2h})$, where the size of the orbit is calculated to be $|D_{4h}|/|D_{2h}| = 16/8 = 2$. Thereby, **7** is determined to belong to the point group D_{2h} , which is identified with the local symmetry of the CR.

D_{4h}							
proper rotations (D_4)							
$I \sim$	$C_4 \sim$	$C_{2(3)} \sim$	$C_4^3 \sim$	$C_{2(1)} \sim$	$C_{2(1)}' \sim$	$C_{2(2)} \sim$	$C_{2(2)}' \sim$
(1)(2)(3)(4)	(1 2 3 4)	(1 3)(2 4)	(1 4 3 2)	(1)(2 4)(3)	(1 2)(3 4)	(1 3)(2)(4)	(1 4)(2 3)
improper rotations							
$\sigma_h \sim$	$S_4 \sim$	$i \sim$	$S_4^3 \sim$	$\sigma_{v(1)} \sim$	$\sigma_{d(1)} \sim$	$\sigma_{v(2)} \sim$	$\sigma_{d(2)} \sim$
(1)(2)(3)(4)	(1 2 3 4)	(1 3)(2 4)	(1 4 3 2)	(1)(2 4)(3)	(1 2)(3 4)	(1 3)(2)(4)	(1 4)(2 3)

Fig. 6. Isomer equivalence for **7** (A^2B^2) under D_{4h}

4.2. *Chiral Complexes and Enantiomeric Relationship.* For chiral molecules of the ligand partition A^2p^2 , Table 2 shows that there are two isomers belonging to D_2 (**9** in Fig. 4) and C''_2 (**25** in Fig. 4). As shown in Fig. 7, **9** is converted to eight homomers and eight enantiomers under D_{4h} . Note that the positions 2 and 4 accommodate a chiral ligand p, while the positions $\bar{2}$ and $\bar{4}$ accommodate the enantiomeric ligand \bar{p} . Since the operations corresponding to D_2 ($=\{I, C_{2(3)}, C_{2(1)}, C_{2(2)}\}$) keep **9** invariant, as shown in Fig. 7, **9** is determined to belong to D_2 symmetry. This process is characterized by the CR $D_{4h}/(D_2)$, which is enantiospheric. This enantiosphericity is confirmed by the comparison of the two sets of homomers (i.e., {**9a**, **9c**, **9e**, **9g**} and {**9b**, **9d**, **9f**, **9h**}) with the two sets of enantiomers (i.e., { $\bar{9a}$, $\bar{9c}$, $\bar{9e}$, $\bar{9g}$ } and { $\bar{9b}$, $\bar{9d}$, $\bar{9f}$, $\bar{9h}$ }). These four sets construct an enantiospheric orbit governed by the CR $D_{4h}/(D_2)$, where the size of the orbit is calculated to be $|D_{4h}|/|D_2|=16/4=4$.

D_{4h}							
proper rotations (D_4)							
$I \sim$	$C_4 \sim$	$C_{2(3)} \sim$	$C_4^3 \sim$	$C_{2(1)} \sim$	$C_{2(1)}' \sim$	$C_{2(2)} \sim$	$C_{2(2)}' \sim$
(1)(2)(3)(4)	(1 2 3 4)	(1 3)(2 4)	(1 4 3 2)	(1)(2 4)(3)	(1 2)(3 4)	(1 3)(2)(4)	(1 4)(2 3)
improper rotations							
$\sigma_h \sim$	$S_4 \sim$	$i \sim$	$S_4^3 \sim$	$\sigma_{v(1)} \sim$	$\sigma_{d(1)} \sim$	$\sigma_{v(2)} \sim$	$\sigma_{d(2)} \sim$
(1)(2)(3)(4)	(1 2 3 4)	(1 3)(2 4)	(1 4 3 2)	(1)(2 4)(3)	(1 2)(3 4)	(1 3)(2)(4)	(1 4)(2 3)

Fig. 7. Isomer equivalence for **9** (A^2p^2) under D_{4h}

4.3. *Prochirality.* A complex is prochiral if it has at least one enantiospheric orbit [8]. According to this criterion, the data listed in Table 1 show that, among the possible achiral subgroups (D_{4h} , D_{2h} , D_{2d} , C_{2h}'' , C_{2h}' , C_{2v}'' , C_{2v}' , C_i , C_s'' , C_s' , and C_s), prochiral complexes are determined to belong to D_{2d} (**8**), C_{2h}'' (**11**), C_{2h}' (**12**), C_i (**16**), C_s' (**21**, **22**, and **23**), and C_s (**24**). They are designated in Fig. 4 by an asterisk added to each compound number.

5. Equivalency under Permutation-Group Symmetry. – 5.1. *Proper and Improper Permutations.* Let us consider the permutation-group symmetry of **7**, which is compared with the point-group symmetry shown in Fig. 6. The permutation group at issue is the symmetric group of degree 4 ($S^{[4]}$), as shown in Eqn. 31. The permutations contained in

$S^{[4]}$ are here classified into proper permutations and improper permutations³⁾. A *proper permutation* is defined as being equal to a permutation contained in the CR that corresponds to the maximal chiral subgroup (D_4) of D_{4h} . Such proper permutations form a permutation group $S_9^{[4]}$, which is isomorphic to D_4 . Permutations other than proper rotations are defined as *improper permutations*. Such improper permutations are involved in the cosets $(1)(243)S_9^{[4]}$ and $(1)(234)S_9^{[4]}$ (Eqn. 31).

As found in Fig. 8, the A^2B^2 complex **7** is converted to homomers by the action of the proper permutations (the top row), while it is converted to diastereoisomers of the same kind (**13a** to **13p**) by the action of improper permutations (the middle and bottom rows). By inspection of the resulting 24 products, the original **7** is fixed into itself (**7a**, **7c**, **7e**, and **7g**) on the action of the following subgroup:

$$S_7^{[4]} = \{(1)(2)(3)(4), (13)(24)(1)(24)(3), (13)(2)(4)\} \quad (33)$$

Thereby, the resulting 24 products are divided into six sets, *i.e.*, {**7a**, **7c**, **7e**, and **7g**}, {**7b**, **7d**, **7f**, and **7h**} (top row); {**13a**, **13c**, **13e**, and **13g**}, {**13b**, **13d**, **13f**, and **13h**} (middle row); {**13i**, **13k**, **13m**, and **13o**}, {**13j**, **13l**, **13n**, and **13p**} (bottom row). The six sets construct an orbit governed by the CR $S^{[4]}/(S_7^{[4]})$, where the size of the orbit is calculated to be $|S^{[4]}|/|S_7^{[4]}| = 24/4 = 6$. This means that **7** and **13** are equivalent under the permutation-group symmetry $S^{[4]}$. Thus a diastereoisomeric relationship such as for **7** and **13** is characterized as an equivalency under a permutation-group symmetry. This conclusion is confirmed by the enumeration result collected in Table 3, where a duplex of **7** and **13** is counted once so that the value 1 appears at the intersection between the A^2B^2 row and the $S_7^{[4]}$ column. The effect of $S^{[4]}$ on the A^2p^2 complex **9** can be discussed in a similar way.

5.2. Stereogenic and Astereogenic Groups. Definition. By virtue of proper and improper permutations, the subgroups of $S^{[4]}$ are classified into two types: *stereogenic* and *astereogenic*. A stereogenic group is defined as a group having proper permutations only, while an astereogenic group is defined as a group having proper and improper permutations. For a given astereogenic group, the *maximal stereogenic subgroup* is defined as a stereogenic subgroup having all the proper permutations of the group. Thus, the subgroup $S_9^{[4]}$ is a maximal stereogenic subgroup of $S^{[4]}$, if we take into account the square-planar skeleton of D_{4h} symmetry. It should be noted that such a maximal stereogenic subgroup depends upon the selection of the skeleton.

Stereogenic Groups. Among the subgroups of the symmetric group $S^{[4]}$, stereogenic groups available for square-planar complexes are determined to be $S_9^{[4]}$, $S_7^{[4]}$, $S_6^{[4]}$, $S_5^{[4]}$, $S_3^{[4]}$, $S_2^{[4]}$, and $S_1^{[4]}$, because each of them contains no improper permutations. However, the enumeration results (Table 3) show that only the subgroups $S_7^{[4]}$, $S_7^{[3]}$, and $S_1^{[4]}$ are capable of generating square-planar complexes.

Since the A^2B^2 complexes described above (**7** and **13**) belong to $S_7^{[4]}$, they are stereogenic so that they are interconvertible (namely, diastereoisomeric) under the permutation-group symmetry $S^{[4]}$. On the same line, the A^2p^2 complexes, **9** and **25**, are ascribed to the stereogenic group $S_7^{[4]}$. In general, the stereogenic group $S_7^{[4]}$ generates a duplex of diastereoisomers such as **7** and **13**. Such duplexes of diastereoisomers as

³⁾ Do not confuse proper and improper permutations with odd and even permutations.

$S^{[4]}$							
proper permutations ($S_9^{[4]}$)							
$I \sim$	$C_4 \sim$	$C_{2(3)} \sim$	$C_4^3 \sim$	$C_{2(1)} \sim$	$C_{2(1)}' \sim$	$C_{2(2)} \sim$	$C_{2(2)}' \sim$
$(1)(2)(3)(4)$	$(1\ 2\ 3\ 4)$	$(1\ 3)(2\ 4)$	$(1\ 4\ 3\ 2)$	$(1)(2\ 4)(3)$	$(1\ 2)(3\ 4)$	$(1\ 3)(2)(4)$	$(1\ 4)(2\ 3)$
improper permutations ($(1)(2\ 4\ 3)S_9^{[4]}$)							
$(1)(2\ 4\ 3)$	$(1\ 4)(2)(3)$	$(1\ 2\ 3)(4)$	$(1\ 3\ 4\ 2)$	$(1)(2\ 3)(4)$	$(1\ 4\ 2)(3)$	$(1\ 2\ 4\ 3)$	$(1\ 3\ 4)(2)$
improper permutations ($(1)(2\ 3\ 4)S_9^{[4]}$)							
$(1)(2\ 3\ 4)$	$(1\ 3\ 2\ 4)$	$(1\ 4\ 3)(2)$	$(1\ 2)(3)(4)$	$(1)(2)(3\ 4)$	$(1\ 3\ 2)(4)$	$(1\ 4\ 2\ 3)$	$(1\ 2\ 4)(3)$

Fig. 8. Isomer equivalence for **7** (A^2B^2) under $S^{[4]}$

assigned to $S_7^{[4]}$ are selected from *Figs. 4* and *5*, as being **{7, 13}**, **{8, 11}**, **{9, 25}**, and **{10, 26}**.

Similarly, the stereogenic group $S_3^{[4]}$ also generates a duplex of diastereoisomers. We select the following duplexes of diastereoisomers assigned to $S_3^{[4]}$ from *Figs. 4* and *5*: **{12, 21}**, **{15, 17}**, **{28, 39}**, **{29, 40}**, **{30, 44}**, **{32, 49}**, **{33, 50}**, **{36, 57}**, **{37, 58}**, and **{38, 59}**.

On the other hand, the stereogenic group $S_1^{[4]}$ generates a triplex of diastereoisomers such as **18, 19**, and **20**. Such triplexes of diastereoisomers as assigned to $S_1^{[4]}$ are selected from *Figs. 4* and *5*, as being **{16, 22, 23}**, **{18, 19, 20}**, **{24, 45, 45}**, **{41, 42, 43}**, **{46, 47, 48}**, **{51, 52, 53}**, **{54, 55, 56}**, **{60, 61, 62}**, and **{63, 64, 65}**. It should be noted that the square-planar complex **45** involved in the triplex **{24, 45, 45}** is not depicted in *Figs. 4* and *5*, since these figures contain a single representative selected from each pair of enantiomers. This means that the relationship between **45** and **45** is recognized as being enantiomeric and, at the same time, as being diastereoisomeric (see below).

Astereogenic Groups. The remaining subgroups, i.e., $S^{[4]}$, $S_{10}^{[4]}$, and $S_8^{[4]}$, $S_4^{[4]}$, are astereogenic in terms of the present criterion. The enumeration results (*Table 3*) show that the subgroups $S^{[4]}$ and $S_8^{[4]}$ are capable of generating square-planar complexes of this type. For $S^{[4]}$, we obtain **5** and **6**. Square-planar complexes of $S_8^{[4]}$ are found to be **14**,

27, **31**, **34**, and **35**, since they contain all the proper and improper permutations of $S_8^{[4]}$. Obviously, each of these complexes is converted to homomers under the action of $S_8^{[4]}$. Hence, it is determined to be astereogenic (*i.e.*, self-diastereomeric) so that it has no diastereoisomer.

5.3. Enantiomeric and Diastereoisomeric Relationships. As described above, point-group symmetry describes chirality/achirality, while permutation-group symmetry corresponds to stereogenicity/astereogenicity. In general, equivalency under point-group symmetry determines an enantiomeric relationship, while equivalency under permutation-group symmetry determines a diastereoisomeric relationship. Although the two relationships can be discussed distinctly in most cases for square-planar complexes, they occasionally overlap and degenerate into one category.

Let us consider the case of **45**, which belongs to the stereogenic group $S_1^{[4]}$. The conversion of **45** under permutation-group symmetry is illustrated in *Fig. 9*. The top row indicates a set of eight homomers (**45a** *etc.*), the middle row shows a set of eight diastereoisomers (**24a**, *etc.*), and the bottom row contains another set of eight diastereoisomers (**45a**, *etc.*). Obviously, the generation of such a triplex of diastereoisomers is in agreement with the general properties of the stereogenic group $S_1^{[4]}$. However, the set of diastereoisomers appearing in the bottom row (**45a**, *etc.*) is at the same time enantiomeric to the set of homomers in the top row (**45a**, *etc.*). Even if a diastereoisomeric relationship and an enantiomeric relationship occasionally overlap, the relationship between **45** and $\overline{\mathbf{45}}$ (and additionally **24**) is diastereoisomeric (and by no means enantiomeric) so long as we rely on the present definition coming from a permutational point of view (*Fig. 9*). However, it is convenient to classify stereogenic molecules by means of the two cases of stereochemical aspect. Thus, if a molecule is converted into its enantiomer under a permutation-group symmetry, it is defined as being *enantiostereogenic* (or shortly, *enantiogenic*); otherwise, it is defined as being *diastereogenic*. In terms of this criterion, **45** is enantiostereogenic and diastereogenic. The complex **24** is also regarded as being enantiostereogenic and diastereogenic, since the action of $S_8^{[4]}$ generates a pair of enantiomers, **45** and $\overline{\mathbf{45}}$.

6. Comparison with Tetrahedral Molecules. – In the present approach, the maximal stereogenic subgroup of a permutation group is selected as being isomorphic to the maximal chiral subgroup of the corresponding point group. This selection stems from our being able to equalize proper rotations (strictly speaking, the corresponding coset representations) and proper permutations, even if chiral ligands are taken into account. The order of the maximal stereogenic subgroup is not always one-half of the order of the permutation group at issue, whereas the order of the maximal chiral subgroup is always one-half of the order of the point group.

For the present case of square-planar complexes, we use D_{4h} as the point group and $S_8^{[4]}$ as the permutation group. Note that D_{4h} is not isomorphic to $S_8^{[4]}$. The order of the maximal chiral subgroup D_4 (order 8) is one-half of the order of D_{4h} (order 16), while the order of the maximal stereogenic subgroup $S_9^{[4]}$ (order 8) is one-third of the order of $S_8^{[4]}$ (order 24).

For the case of tetrahedral molecules, on the other hand, we have used T_d (order 24) as the point group and the same $S_8^{[4]}$ (order 24) as the permutation group [26]. Note that T_d is isomorphic to $S_8^{[4]}$. Hence, we have considered the maximal chiral subgroup T

$S^{[4]}$							
proper permutations ($S_9^{[4]}$)							
$I \sim$	$C_4 \sim$	$C_{2(3)} \sim$	$C_4^3 \sim$	$C_{2(1)} \sim$	$C_{2(1)}' \sim$	$C_{2(2)} \sim$	$C_{2(2)}' \sim$
(1)(2)(3)(4)	(1 2 3 4)	(1 3)(2 4)	(1 4 3 2)	(1)(2 4)(3)	(1 2)(3 4)	(1 3)(2)(4)	(1 4)(2 3)
improper permutations ($(1)(2 4 3)S_9^{[4]}$)							
(1)(2 4 3)	(1 4)(2)(3)	(1 2 3)(4)	(1 3 4 2)	(1)(2 3)(4)	(1 4 2)(3)	(1 2 4 3)	(1 3 4)(2)
improper permutations ($(1)(2 3 4)S_9^{[4]}$)							
(1)(2 3 4)	(1 3 2 4)	(1 4 3)(2)	(1 2)(3)(4)	(1)(2)(3 4)	(1 3 2)(4)	(1 4 2 3)	(1 2 4)(3)

Fig. 9. Isomer equivalence for **45** (ABp̄p̄) under $S^{[4]}$

(order 12) vs. the point group T_d (order 24); and the maximal stereogenic subgroup $S_{10}^{[4]}$ (order 12) vs. the point group $S^{[4]}$ (order 24). This feature has enabled us to discuss enantiomeric and diastereoisomeric relationships in terms of the observance and violation of chirality fittingness, where T_d and $S^{[4]}$ have been regarded as the same abstract group but have been differentiated by taking account of chirality fittingness.

Whether a given molecule is stereogenic or astereogenic depends upon the selection of the maximal permutational subgroup. This provides us with a solution for the question described for Fig. 1. The A^2B^2 molecule (**1**) based on a tetrahedral skeleton is characterized by $S_7^{[4]}$, which is astereogenic under the maximal permutation subgroups $S_{10}^{[4]}$. Hence, it has no diastereoisomer. The A^2B^2 molecule (**2**) based on a square-planar skeleton is characterized by the same $S_7^{[4]}$; however, it is determined to be stereogenic, since the maximal permutational subgroup $S_9^{[4]}$ is taken into consideration in the present paper. Hence, it has the corresponding diastereoisomer (**3**).

7. Conclusions. – Square-planar complexes with achiral and chiral ligands are combinatorially enumerated under the point-group D_{4h} , where its mark table and its inverse mark table are prepared and used to calculate the subduction of coset representations. The enumeration results, which are itemized with formulas and point-

group symmetries, are used to discuss equivalency under point-group symmetry, *e.g.*, enantiomeric relationships for chiral complexes and prochirality for achiral complexes. The combinatorial enumeration of the square-planar complexes are alternatively carried out under the permutation-group $S^{[4]}$, which is the symmetric group of degree 4. After the definition of proper and improper permutations, the subgroups of $S^{[4]}$ are classified into stereogenic and astereogenic groups for square-planar complexes. Thereby, equivalency under permutation-group symmetry is discussed to clarify enantiomeric and diastereoisomeric relationships. The comparison between the action of a point group and that of a permutation group provides us a new and versatile methodology for restructuring stereochemistry.

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