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Enumeration of Conformers for Octahedral *cis*/*trans*-[$MX_4(AB)_2$] and *cis*/*trans*-[$MX_4(ABC)_2$] Complexes on the Basis of Computational Group Theory

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Abstract

Conformers of *cis*-[$MX_4(AB)_2$], *trans*-[$MX_4(AB)_2$], *cis*-[$MX_4(ABC)_2$], and *trans*-[$MX_4(ABC)_2$] complexes have been enumerated on the basis of computational group theory, where M, X, AB, and ABC are the central metal ion, the monoatomic ligand, the diatomic ligand possessing donor atom A, and the bent triatomic ligand possessing donor atom A, respectively. For the *cis*-[$MX_4(AB)_2$] complex, five bisected diastereomers have been found as 2 C_2, 1 C_s, 2 C_1. Based on the five diastereomers of the *cis*-$MX_4(AB)_2$ core unit, 36 diastereomers have been found for the *cis*-[$MX_4(ABC)_2$] complex, which are assigned to three-point groups, 6 C_2, 3 C_s, 27 C_1. On the other hand, for the *trans*-[$MX_4(AB)_2$] complex, three bisected diastereomers have been found as 1 C_{2h}, 1 C_{2v}, 1 C_2. Based on the three diastereomers of the *trans*-$MX_4(AB)_2$ core unit, 14 diastereomers have been found for the *trans*-[$MX_4(ABC)_2$] complex, which are assigned to six-point groups, 1 C_{2h}, 1 C_{2v}, 5 C_2, 1 C_s, 1 C_i, 5 C_1. Enumeration results are expected to be useful in conformational analysis of related metal complexes.

1 Introduction

Conformational analysis is one of the reliable methods in predicting structures of flexible molecules, and enumeration of the conformers is important as the first step of conformational analysis. For metal complexes, enumeration is not so easy because of the large number of conformers caused by the branches at the central metal, but once the conformers of typical

structures are enumerated, the relating complexes have the same enumeration results. The conformers of octahedral metal complexes have been enumerated for several types of complexes, including [M(AB)$_6$], [M(ABC)$_6$], [MX(AB)$_5$], [MX(ABC)$_5$], *cis/trans*-[MX$_2$(AB)$_4$], *cis/trans*-[MX$_2$(ABC)$_4$], *fac*/*mer*-[MX$_3$(AB)$_3$], and *fac*/*mer*-[MX$_3$(ABC)$_3$] [1-7], by the computational group theory (CGT) method [8], where M, X, AB, and ABC are the central metal, the monoatomic ligand, the diatomic ligand possessing donor atom A, and the bent triatomic ligand possessing donor atom A, respectively. Conformational analysis was shown to be useful [1,2,9,10] not only for predicting the stable structures but also for interpreting physicochemical properties (*e.g.* phase-transition behavior), using the result of the enumeration.

In this study, in order to extend the target molecules in the conformational analysis, enumeration was conducted for octahedral complexes, *cis*-[MX$_4$(AB)$_2$], *trans*-[MX$_4$(AB)$_2$], *cis*-[MX$_4$(ABC)$_2$], and *trans*-[MX$_4$(ABC)$_2$] (Figure 1), possessing two AB or ABC ligands. This study will be the last one of this enumeration series, because the [MX$_5$(AB)] and [MX$_5$(ABC)] complexes are too simple to be discussed. The *cis*-complexes possess central *cis*-MX$_4$A$_2$ unit, belonging to the C_{2v} point group, while the *trans*-complexes possess central *trans*-MX$_4$A$_2$ unit, belonging to the D_{4h} point group. The enumeration results are expected to be useful for conformational analysis for related octahedral complexes.

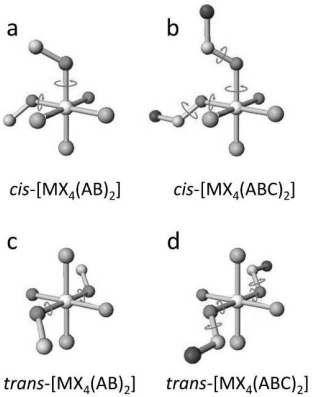

Figure 1. Structures of octahedral metal complexes, *cis*-[MX$_4$(AB)$_2$] (a), *cis*-[MX$_4$(ABC)$_2$] (b), *trans*-[MX$_4$(AB)$_2$] (c), and *trans*-[MX$_4$(ABC)$_2$] (d)

2 Methods

Conformers were obtained based on the computational group theory (CGT) method [7], which was performed using GAP program [11] on Intel Core i5-2450 (2.50GHz) computer. Three-dimensional models were drawn by Winmostar software [12], and the point groups were ascertained by the software. In enumeration, four bisecting orientations are considered for the rotation around the M-A bond, and three orientations are considered for the rotation around the A-B bond (Figure 2a). To describe the structure, we use the following notation [1-7]. For example, the structure shown in Figure 2b is described as [[y + z], [-], [-], [-], [-], [- x - y]]. In this notation, the orientations of the AB ligands are described as [y + z], [- x – y], etc., and the X ligands are described as [-], in the order of the numbering system [x, y, z, -x, -y, -z].

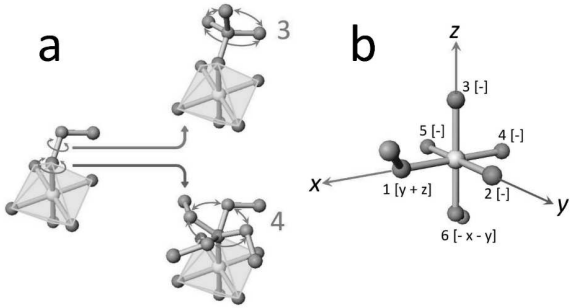

Figure 2. Typical orientations considered in enumeration (a) and an example of a conformer with a numbering system (b)

3 Results and discussion

3.1 Enumeration for *cis*- and *trans*-[$MX_4(AB)_2$] complexes

The enumeration was conducted for the *cis*- and *trans*-[$MX_4(AB)_2$] complexes, excluding the unfavorable structures possessing B atoms in a close distance. The resulting diastereomers are summarized in Table 1 with their point groups and are depicted in Figure 3. The obtained five diastereomers, L2-C1 – L2-C5, are categorized in three-point groups as 2 C_2, 1 C_s, 2 C_1. Here,

"L2" means the complex possesses two flexible ligand-arms. Since the C_2 and C_1 point groups are chiral among the three-point groups, each diastereomer belonging to either the C_2 or C_1 point group has an enantiomer. Therefore, the total number of conformers is nine (L2-C1, L2-C1', L2-C2, L2-C2', L2-C3, L2-C4, L2-C4', L2-C5, and L2-C5', where the symbol " ' " represents the mirror image). Except for the C_1 point group, each of the appeared point group belongs to a subgroup of the C_{2v} point group, to which the *cis*-MX_4A_2 coordination geometry belongs.

Table 1. Bisecting diastereomers for a *cis*-$[MX_4(AB)_2]$ complex

No	Example	Point Group
L2-C1	[[y + z], [-], [-], [-], [-], [– x – y]]	C_2
L2-C2	[[y + z], [-], [x – y], [-], [-], [-]]	C_2
L2-C3	[[y + z], [-], [-], [-], [– x + z], [-]]	C_s
L2-C4	[[y + z], [-], [– x + y], [-], [-], [-]]	C_1
L2-C5	[[y + z], [-], [– x – y], [-], [-], [-]]	C_1

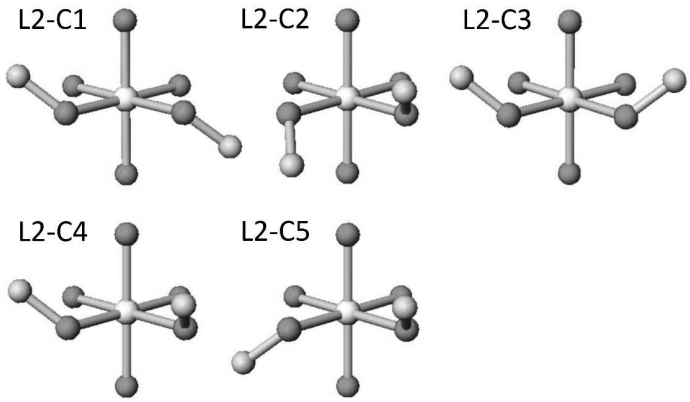

Figure 3. Structures of diastereomers L2-C1 – L2-C5

The enumeration for the *trans*-[$MX_4(AB)_2$] complex was conducted in the same way, and the resulting diastereomers are summarized in Table 2 with their point groups and are depicted in Figure 4. The obtained three diastereomers, L2-T1 – L2-T3, are categorized in three-point groups as 1 C_{2h}, 1 C_{2v}, 1 C_2. Among them, the C_2 point group is chiral, and the diastereomer belonging to the C_2 point group has an enantiomer. Total number of the conformers is four (L2-T1, L2-T2, L2-T3, and L2-T3', where the symbol " ' " represents the mirror image). Each of the appeared point group belongs to a subgroup of the D_{4h} point group, to which the *trans*-MX_4A_2 coordination geometry belongs.

Table 2. Bisecting diastereomers for a *trans*-[$MX_4(AB)_2$] complex

No	Example	Point Group
L2-T1	[[y + z], [-], [-], [– y – z], [-], [-]]	C_{2h}
L2-T2	[[y + z], [-], [-], [y + z], [-], [-]]	C_{2v}
L2-T3	[[y + z], [-], [-], [– y + z], [-], [-]]	C_2

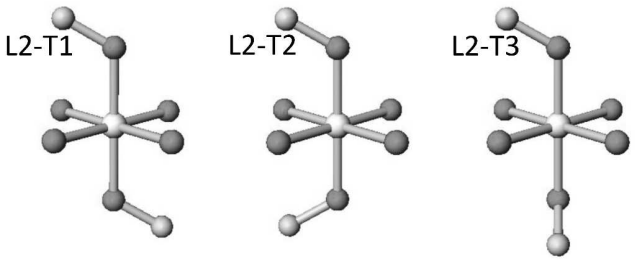

Figure 4. Structures of diastereomers L2-T1 – L2-T3

3.2 Enumeration for *cis*-[$MX_4(ABC)_2$] complex

Conformers of *cis*-[$MX_4(ABC)_2$] complex were considered using the enumeration result of *cis*-[$MX_4(AB)_2$] complex. Based on the *cis*-$MX_4(AB)_2$ unit, each ligand, AB, was extended from atom B to atom C to consider the conformers of *cis*-[$MX_4(ABC)_2$] complex. For the extension of C, three directions were considered whose dihedral angles M-A-B-C were 180° (anti conformer), 300° (gauche conformer), and 60° (gauche conformer) (Figure 2a). This is thought to be sufficient for the purpose of conformational analysis. The resulting diastereomers are summarized in Table 3. The total number of diastereomers becomes 36, including 6 C_2, 3 C_s, 27 C_1 diastereomers, as listed in Table 4. Since the C_2 and C_1 point groups are chiral, the number of conformers becomes 69 in total, including 12 C_2, 3 C_s, 54 C_1 conformers. Except for the C_1 point group, all the point groups belong to the subgroups of the C_{2v} point group, to which the *cis*-MX_4A_2 unit belongs.

Table 3. Bisecting diastereomers of *cis*-[$MX_4(ABC)_2$], derived from *cis*-$MX_4(AB)_2$ core unit

No	Point group of *cis*-$MX_4(AB)_2$ core unit	Point groups of *cis*-[$MX_4(ABC)_2$] diastereomer	Total number of diastereomers	Total number of conformers
L2-C1	C_2	3 C_2, 3 C_1	6	12
L2-C2	C_2	3 C_2, 3 C_1	6	12
L2-C3	C_s	3 C_s, 3 C_1	6	9
L2-C4	C_1	9 C_1	9	18
L2-C5	C_1	9 C_1	9	18
		Total	36	69

Table 4. Bisecting conformers of *cis*-[$MX_4(ABC)_2$]

No	Point group	Total number of diastereomers	Total number of conformers
1	C_2	6	12
2	C_s	3	3
3	C_1	27	54
	Total	36	69

3.3 Enumeration for *trans*-[$MX_4(ABC)_2$] complex

Conformers of *trans*-[$MX_4(ABC)_2$] complex were considered using the enumeration result of *trans*-[$MX_4(AB)_2$] complex, and the resulting diastereomers are summarized in Table 5. The total number of diastereomers becomes 14, including 1 C_{2h}, 1 C_{2v}, 5 C_2, 1 C_s, 1 C_i, 5 C_1 diastereomers, as listed in Table 6. Since the C_2 and C_1 point groups are chiral, the total number of conformers becomes 24, including 1 C_{2h}, 1 C_{2v}, 10 C_2, 1 C_s, 1 C_i, 10 C_1 conformers. Except for the C_1 point group, all the point groups belong to the subgroups of the D_{4h} point group, to which the *trans*-MX_4A_2 unit belongs.

Table 5. Bisecting diastereomers of *trans*-[$MX_4(ABC)_2$], derived from *trans*-$MX_4(AB)_2$ core unit

No	Point group of *trans*-$MX_4(AB)_2$ core unit	Point groups of *trans*-[$MX_4(ABC)_2$] diastereomer	Total number of diastereomers	Total number of conformers
L2-T1	C_{2h}	1 C_{2h}, 1 C_2, 1 C_i, 1 C_1	4	6
L2-T2	C_{2v}	1 C_{2v}, 1 C_2, 1 C_s, 1 C_1	4	6
L2-T3	C_2	3 C_2, 3 C_1	6	12
		Total	14	24

Table 6. Bisecting conformers of *trans*-[$MX_4(ABC)_2$]

No	Point group	Total number of diastereomers	Total number of conformers
1	C_{2h}	1	1
2	C_{2v}	1	1
3	C_2	5	10
4	C_s	1	1
5	C_i	1	1
6	C_1	5	10
	Total	14	24

As summarized in Tables 1-6, possible diastereomers are enumerated for *cis*/*trans*-[$MX_4(AB)_2$] and *cis*/*trans*-[$MX_4(ABC)_2$] complexes. This kind of enumeration results were recently found to be useful not only for predicting the structures, but also for understanding the phase-transition behavior of metal complexes [10]. The enumeration results in this study is also expected to be useful in the future.

4 Concluding remarks

In this study, conformers of octahedral *cis*/*trans*-$[MX_4(AB)_2]$ and *cis*/*trans*-$[MX_4(ABC)_2]$ complexes were enumerated on the basis of computational group theory. For the *cis*-$[MX_4(AB)_2]$ complex, five bisecting diastereomers have been found as 2 C_2, 1 C_s, 2 C_1. For the *cis*-$[MX_4(ABC)_2]$ complex, 36 bisecting diastereomers have been found as 6 C_2, 3 C_s, 27 C_1. For the *trans*-$[MX_4(AB)_2]$ complex, three bisecting diastereomers have been found as 1 C_{2h}, 1 C_{2v}, 1 C_2. For the *trans*-$[MX_4(AB)_2]$ complex, 14 bisecting diastereomers have been found as 1 C_{2h}, 1 C_{2v}, 5 C_2, 1 C_s, 1 C_i, 5 C_1. The results were summarized in tables, which are useful in conformational analysis of the related metal complexes.

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