MATCH
Communications in Mathematical and in Computer Chemistry

MATCH Commun. Math. Comput. Chem. **81** (2019) 593-602

ISSN 0340 - 6253

Enumeration of Conformers for Octahedral *fac*/*mer*-[$MX_3(AB)_3$] and *fac*/*mer*-[$MX_3(ABC)_3$] Complexes on the Basis of Computational Group Theory*

Hiroshi Sakiyama†, Katsushi Waki

Department of Science, Faculty of Science, Yamagata University, Japan

Kojirakawa 1-4 12, Yamagata 990-8560, Japan

saki@sci.kj.yamagata-u.ac.jp

(Received August 27, 2018)

Abstract

Conformers of *fac*-[MX3(AB)3], *mer*-[MX3(AB)3], *fac*-[MX3(ABC)3], and *mer*-[MX3(ABC)3] complexes have been enumerated on the basis of computational group theory, where M is the central metal ion, while X, AB, and ABC are the monoatomic, diatomic, and bent triatomic ligands, respectively, bound to M through X or A. For the *fac*-[MX3(AB)3] complex, 10 bisected diastereomers have been found as 1 *C*3*v*, 1 *C*3, 3 *Cs*, and 5 *C*1. Based on the 10 diastereomers of the *fac*-MX3(AB)3 core unit, 198 diastereomers have been found for the *fac*-[MX3(ABC)3] complex, which are assigned to six point groups, 1 *C*3*v*, 4 *C*3, 11 *Cs*, 182 *C*1. On the other hand, for the *mer*-[MX3(AB)3] complex, 12 bisected diastereomers have been found as 12 *C*1. Based on the 12 diastereomers of the *mer*-MX3(AB)3 core unit, 324

* This work was supported by JSPS KAKENHI Grant Number 15K05445.
† Corresponding author

diastereomers have been found for the *mer*-[$MX_3(ABC)_3$] complex, which are assigned to the C_1 point group as 324 C_1.

1 Introduction

Enumeration of the conformers is of importance in conformational analysis. For metal complexes, however, enumeration is not so easy because of the large number of conformers due to the large coordination numbers. The conformers of octahedral metal complexes, [$M(AB)_6$], [$M(ABC)_6$], [$MX(AB)_5$], [$MX(ABC)_5$], *trans*-[$MX_2(AB)_4$], *trans*-[$MX_2(ABC)_4$], *cis*-[$MX_2(AB)_4$], and *cis*-[$MX_2(ABC)_4$] (Figure 1), have been enumerated [1-6] by the computational group theory (CGT) method [7], where M is the central metal ion, while X, AB, and ABC are the monoatomic, diatomic, and bent triatomic ligands, respectively, bound to M through X or A. Using the result of the enumeration, conformational analysis was conducted for some actual compounds [1,2,8].

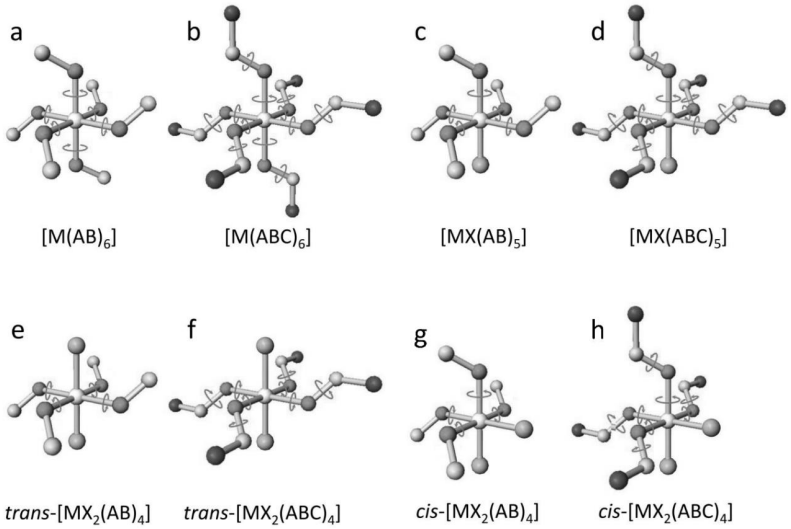

Figure 1. Structures of octahedral metal complexes, [$M(AB)_6$] (a), [$M(ABC)_6$] (b), [$MX(AB)_5$] (c), [$MX(ABC)_5$] (d), *trans*-[$MX_2(AB)_4$] (e), *trans*-[$MX_2(ABC)_4$] (f), *cis*-[$MX_2(AB)_4$] (g), and *cis*-[$MX_2(ABC)_4$] (h)

In this study, in order to extend the target molecules in the conformational analysis, enumeration was conducted for octahedral complexes, *fac*-[$MX_3(AB)_3$], *mer*-[$MX_3(AB)_3$], *fac*-[$MX_3(ABC)_3$], and *mer*-[$MX_3(ABC)_3$] (Figure 2). The *fac*-complexes possess central *fac*-MX_3A_3 unit, belonging to the C_{3v} point group, while the *mer*-complexes possess central *mer*-MX_3A_3 unit, belonging to the C_{2v} point group. The enumeration results are expected to be useful for conformational analysis for related octahedral complexes.

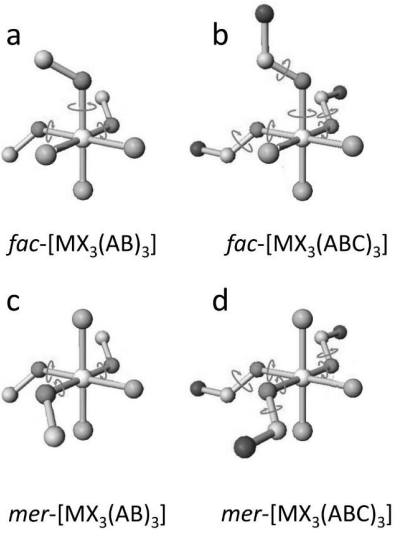

Figure 2. Structures of octahedral metal complexes, *fac*-[$MX_3(AB)_3$] (a), *fac*-[$MX_3(ABC)_3$] (b), *mer*-[$MX_3(AB)_3$] (c), and *mer*-[$MX_3(ABC)_3$] (d)

2 Methods

Conformers were obtained based on the computational group theory (CGT) method [7], which was performed using GAP program [9] on Intel Core i5-2450 (2.50GHz) computer. Three-dimensional models were drawn by Winmostar software [10], and the point groups were ascertained by the software. In enumeration, four orientations (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 3a). To describe the structure, we use the following notation [1-6]. For example, the structure shown in Figure 3b is described as [[y + z], [-], [-], [-], [- x + z], [- x + y]]. In this notation, the orientations of the AB ligands are described as [y+z], [-x+z], etc., and the X ligands are described as [-], in the order of the numbering system [x, y, z, -x, -y, -z].

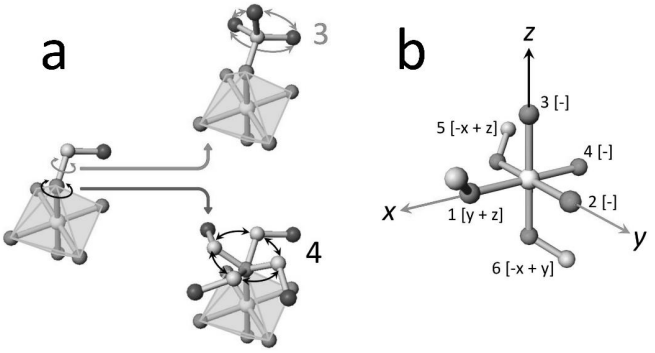

Figure 3. Typical orientations considered in enumeration (a) and an example of a conformer with a numbering system (b)

3 Results and discussion

3.1 Enumeration for *fac*- and *mer*-[$MX_3(AB)_3$] complex

The enumeration was conducted for the *fac*-[$MX_3(AB)_3$] complex by the GAP program [9], 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 4. The obtained 10 diastereomers, F1-F10, are categorized in four-point groups as 1 C_{3v}, 1 C_3, 3 C_s and 5 C_1. Among them, the C_3 and C_1 point groups are chiral. So, each diastereomer belonging to either the C_3 or C_1 point group has an enantiomer, and the total number of the conformers is 16. (F1, F2, F2', F3, F4, F5, F6, F6', F7, F7', F8, F8', F9, F9', F10, and F10', where the symbol " ' " represents the mirror image). Except for the C_1 point group, all the point

groups belong to the subgroups of the C_{3v} point group. This is consistent with the C_{3v} symmetry of the *fac*-MX_3A_3 coordination geometry.

Table 1. Bisecting diastereomers for a *fac*-[$MX_3(AB)_3$] complex

No	Example	Point Group
F1	[[y + z], [-], [-], [-], [- x + z], [- x + y]]	C_{3v}
F2	[[y + z], [-], [- x - y], [-], [x - z], [-]]	C_3
F3	[[y + z], [-], [x - y], [-], [- x + z], [-]]	C_s
F4	[[y + z], [-], [- x + y], [-], [- x + z], [-]]	C_s
F5	[[y + z], [-], [-], [-], [- x + z], [x - y]]	C_s
F6	[[y + z], [-], [-], [-], [- x + z], [- x - y]]	C_1
F7	[[y + z], [-], [- x - y], [-], [x + z], [-]]	C_1
F8	[[y + z], [-], [x - y], [-], [- x - z], [-]]	C_1
F9	[[y + z], [- x - z], [- x + y], [-], [-], [-]]	C_1
F10	[[y + z], [- x - z], [-], [-], [-], [- x - y]]	C_1

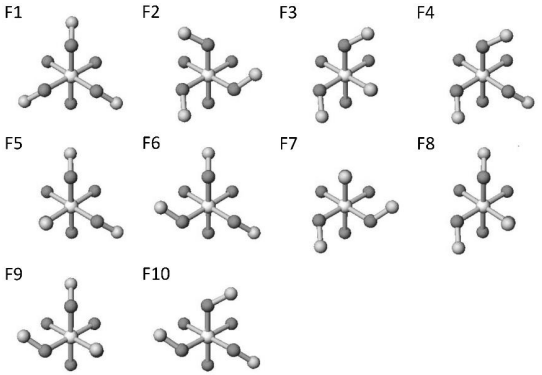

Figure 4. Structures of diastereomers F1-F10

The enumeration for the *mer*-[$MX_3(AB)_3$] 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 5. Although the central *mer*-MX_3A_3 unit belongs to the C_{2v} point group; however, since we consider the bisecting orientations for the A-B bond, all of the obtained 12 diastereomers,

M1-M12, belong to the C_1 point group (12 C_1). Since the C_1 point group is chiral, the total number of the conformers is 24, considering the enantiomers.

Table 2. Bisecting diastereomers for a *mer*-[$MX_3(AB)_3$] complex

No	Example	Point Group
M1	[[y + z], [-], [- x + y], [-], [-], [- x + y]]	C_1
M2	[[y + z], [-], [- x + y], [- y + z], [-], [-]]	C_1
M3	[[y + z], [-], [x - y], [-], [-], [x - y]]	C_1
M4	[[y + z], [-], [x - y], [-], [-], [- x - y]]	C_1
M5	[[y + z], [-], [-], [- y - z], [- x + z], [-]]	C_1
M6	[[y + z], [- x + z], [-], [- y + z], [-], [-]]	C_1
M7	[[y + z], [- x + z], [-], [-], [- x - z], [-]]	C_1
M8	[[y + z], [-], [- x - y], [- y - z], [-], [-]]	C_1
M9	[[y + z], [- x + z], [-], [- y - z], [-], [-]]	C_1
M10	[[y + z], [-], [- x - y], [-], [-], [- x - y]]	C_1
M11	[[y + z], [- x - z], [-], [- y + z], [-], [-]]	C_1
M12	[[y + z], [-], [- x - y], [-], [-], [- x + y]]	C_1

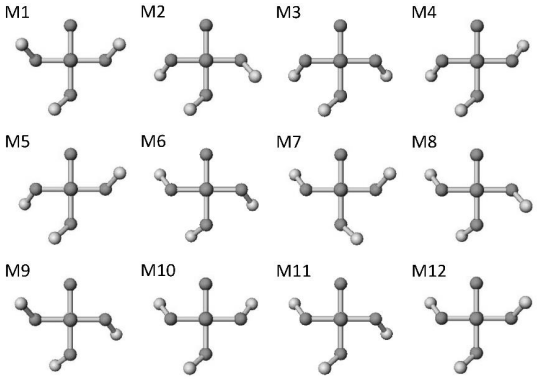

Figure 5. Structures of diastereomers M1-M12

3.2 Enumeration for *fac*-[$MX_3(ABC)_3$] complex

Conformers of *fac*-[$MX_3(ABC)_3$] complex were considered using the enumeration result of *fac*-[$MX_3(AB)_3$] complex. Based on the *fac*-$MX_3(AB)_3$ unit, each ligand, AB, was extended from atom B to atom C to consider the conformers of *fac*-[$MX_3(ABC)_3$] 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). This is thought to be sufficient for the purpose of conformational analysis. The resulting diastereomers for the *fac*-[$MX_3(ABC)_3$] complex are summarized in Table 3. Generally, 3^3 (= 27) conformers are expected to be generated from each diastereomer for the *fac*-$MX_3(AB)_3$ unit, by the extension of the ligands; however, in the case of *fac*-$MX_3(AB)_3$ unit of C_{3v} point group, for example, the conformers are categorized in 7 diastereomers, including 1 C_{3v}, 1 C_3, 2 C_s, and 3 C_1 diastereomers. On the other hand, in the case of *fac*-$MX_3(AB)_3$ unit of C_1 point group, there are 27 diastereomers, belonging to C_1 point group. Consequently, the number of diastereomers becomes 198 in total, including 1 C_{3v}, 4 C_3, 11 C_s, and 182 C_1 diastereomers, as listed in Table 4. Since the C_3 and C_1 point groups are chiral, the number of conformers becomes 384 in total, including 1 C_{3v}, 8 C_3, 11 C_s, and 364 C_1 conformers. Except for the C_1 point group, all the point groups belong to the subgroups of the C_{3v} point group, to which the *fac*-MX_3A_3 unit belongs.

Table 3. Bisecting diastereomers of *fac*-[$MX_3(ABC)_3$], derived from *fac*-$MX_3(AB)_3$ core unit

No	Point group of *fac*-$MX_3(AB)_3$ core unit	Point groups of *fac*-[$MX_3(ABC)_3$] diastereomer	Total number of diastereomers	Total number of conformers
F1	C_{3v}	1 C_{3v}, 1 C_3, 2 C_s, 3 C_1	7	11
F2	C_3	3 C_3, 8 C_1	11	22
F3	C_s	3 C_s, 12 C_1	15	27
F4	C_s	3 C_s, 12 C_1	15	27
F5	C_s	3 C_s, 12 C_1	15	27
F6	C_1	27 C_1	27	54
F7	C_1	27 C_1	27	54
F8	C_1	27 C_1	27	54
F9	C_1	27 C_1	27	54
F10	C_1	27 C_1	27	54
		Total	198	384

Table 4. Bisecting conformers of *fac*-[$MX_3(ABC)_3$]

No	Point group	Total number of diastereomers	Total number of conformers
1	C_{3v}	1	1
2	C_3	4	8
3	C_s	11	11
4	C_1	182	364
	Total	198	384

3.3 Enumeration for *mer*-[$MX_3(ABC)_3$] complex

Conformers of *mer*-[$MX_3(ABC)_3$] complex were considered using the enumeration result of *mer*-[$MX_3(AB)_3$] complex, and the resulting diastereomers are summarized in Table 5. The number of diastereomers is 324 in total, corresponding 324 C_1 diastereomers, as listed in Table 6. Since the C_1 point group is chiral, the number of conformers becomes 648 in total.

Table 5. Bisecting diastereomers of *mer*-[$MX_3(ABC)_3$], derived from *mer*-$MX_3(AB)_3$ core unit

No	Point group of *mer*-$MX_3(AB)_3$ core unit	Point groups of *mer*-[$MX_3(ABC)_3$] diastereomer	Total number of diastereomers	Total number of conformers
M1	C_1	27 C_1	27	54
M2	C_1	27 C_1	27	54
M3	C_1	27 C_1	27	54
M4	C_1	27 C_1	27	54
M5	C_1	27 C_1	27	54
M6	C_1	27 C_1	27	54
M7	C_1	27 C_1	27	54
M8	C_1	27 C_1	27	54
M9	C_1	27 C_1	27	54
M10	C_1	27 C_1	27	54
M11	C_1	27 C_1	27	54
M12	C_1	27 C_1	27	54
		Total	324	648

Table 6. Bisecting conformers of *mer*-[$MX_3(ABC)_3$]

No	Point group	Total number of diastereomers	Total number of conformers
1	C_1	324	648
	Total	324	648

As summarized in Tables 1-6, possible diastereomers are enumerated for *fac*/*mer*-[$MX_3(AB)_3$] and *fac*/*mer*-[$MX_3(ABC)_3$] complexes. As the previous enumeration results [1-3] were useful for the conformational analyses of some metal complexes [1,2,8], the enumeration results in this study are expected to be useful for conformational analysis of related octahedral complexes.

4 Concluding remarks

In this study, conformers of octahedral fac/mer-[MX3(AB)3] and fac/mer-[MX3(ABC)3] complexes were enumerated on the basis of computational group theory. For the fac-[MX3(AB)3] complex, 10 bisecting diastereomers have been found as 1 C3v, 1 C3, 3 Cs and 5 C1. For the fac-[MX3(ABC)3] complex, 198 bisecting diastereomers have been found as 1 C3v, 4 C3, 11 Cs, and 182 C1. For the mer-[MX3(AB)3] complex, 12 bisecting diastereomers have been found as 12 C1. For the mer-[MX3(AB)3] complex, 324 bisecting diastereomers have been found as 324 C1. The results were summarized in tables, which are useful in conformational analysis of the related complexes.

Acknowledgement: Financial support by Yamagata University is acknowledged.

References

[1] H. Sakiyama, K. Waki, Conformational analysis of hexakis-methylamine nickel(II) complex on the basis of computational group theory and density functional theory, *J. Comput. Chem. Jpn.* **13** (2014) 223–228.

[2] H. Sakiyama, K. Waki, Conformational analysis of hexakis-N-methylformamide nickel(II) complex on the basis of computational group theory and density functional theory, *J. Comput. Chem. Jpn. Int. Ed.* **1** (2015) 5–8.

[3] H. Sakiyama, K. Waki, Enumeration of conformers of octahedral [M(ABC)$_6$] complex on the basis of computational group theory, *Iranian J. Math. Chem.* **7** (2016) 223–234.

[4] H. Sakiyama, K. Waki, Enumeration of conformers for octahedral [MX(AB)$_5$] and [MX(ABC)$_5$] complexes on the basis of computational group theory, *J. Math. Chem.* **55** (2017) 1360–1366.

[5] H. Sakiyama, K. Waki, Enumeration of conformers for octahedral trans/cis-[MX$_2$(AB)$_4$] and trans/cis-[MX$_2$(ABC)$_4$] complexes on the basis of computational group theory, *J. Math. Chem.* (2018), in press.

[6] H. Sakiyama, K. Waki, Enumeration of edge-oriented conformers of octahedral [M(ABC)$_6$] complex on the basis of computational group theory, *MATCH Commun. Math. Comput. Chem.* (2019), in press.

[7] D. F. Holt, *Handbook of Computational Group Theory*, Chapman & Hall, Boca Raton, 2005.

[8] H. Sakiyama, T. Abiko, M. Ito, R. Mitsuhashi, M. Mikuriya, K. Waki, Conformational analysis of an octahedral zinc(II) complex with six dimethylsulfoxide, *Polyhedron* **119** (2016) 512–516.

[9] The GAP Group, GAP-Groups, Algorithms, and Programming, Version 4.7.9; 2015. (http://www.gap-system.org)

[10] X-Ability Co., Ltd., Winmostar Software, Version 7.025; 2017. (http://winmostar.com)