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Enumeration of Conformers for Tetrahedral $[MX_{4-n}(AB)_n]$ Complexes (n = 1–4)

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Abstract

Conformers of tetrahedral $[MX_{4-n}(AB)_n]$ (n = 1 – 4) complexes have been enumerated on the basis of the group theory method, where M, X, and AB are the central metal atom, monoatomic ligand, and the diatomic ligand with a donor atom A, respectively. The AB ligand is assumed to coordinate to the metal ion in a bending form. The enumeration was conducted for the bisecting conformers, in which the AB ligands bend toward the bisecting directions of the tetrahedral coordination geometry, but the edge-orienting conformers can be generated by rotating the M-A bonds by 180°. The enumeration result is useful for considering various types of tetrahedral metal complexes by replacing the X and AB ligands. For example, a rigid dimethylformamide (Me_2NCHO) ligand can be introduced by replacing the A and B atoms with O and N atoms of the dimethylformamide ligand.

1 Introduction

Flexible molecules change their shape and become various conformer structures. Especially in solution, some flexible molecules are in equilibrium between multiple conformers. The simplest method to represent this state is to show the most stable conformer. Another way is to show some conformer structures along with their abundance. Further detail method may be also possible, but in any case, the description of the state is helpful in understanding the behavior of the molecules. We have been tackling this challenge [1–5] with the use of enumeration result for several types of octahedral complexes [6–13], and this method can find the conformers efficiently, because the conformers are exhaustively obtained without duplication. Since some

results have been successfully obtained with the octahedral complexes, in this study, enumeration study is conducted for some tetrahedral complexes. To date excellent enumeration studies have been reported for tetrahedral organic molecules [14–17]. In this article, enumeration is conducted with the aim of enabling conformational analysis of tetrahedral metal complexes. The result is expected to be useful in understanding the properties of tetrahedral lithium complexes in electrolyte solutions of lithium-ion batteries [18,19].

In this study, conformers of tetrahedral $[MX_{4-n}(AB)_n]$ (n = 1 – 4) complexes are enumerated on the basis of the group theory method, where M, X, and AB are the central metal atom, monoatomic ligand, and the diatomic ligand with a donor atom A, respectively. The AB ligand is assumed to coordinate to the metal ion in a bending form (Figure 1). Although the AB is a diatomic ligand, the enumeration result is expected to be useful not for the diatomic ligands but also various types of rigid monodentate ligands. For example, a rigid dimethylformamide (Me_2NCHO) ligand can be introduced by replacing the A and B atoms with O and N atoms of the dimethylformamide ligand.

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Figure 1. Coordination mode for the AB ligand.

For the AB ligand in the bending coordination mode, there are two typical orientations on the tetrahedral coordination geometry: edge orientation and bisecting orientation (Figure 2). The edge orientation corresponds to the eclipsed form and the bisecting orientation to the staggered form. Since the eclipsed forms are generally not favorable, the bisecting orientations (staggered forms) are mainly going to be considered. However, if necessary, the edge-orienting conformers can be obtained from the bisecting conformers by rotating all of the AB ligands by 180° around the M-A bonds.

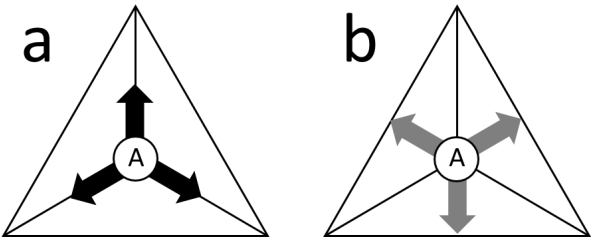

Figure 2. Typical orientations with respect to the tetrahedral coordination geometry: edge orientations (a) and bisecting orientations (b).

2 Methods

Three-dimensional models were handled by Winmostar software [20], and the point groups were confirmed by the software. The enumeration of the conformers was conducted on the basis of the group theory method. The enumeration algorithm is described in reference 21, and the enumeration was conducted manually. The completeness of enumerations was confirmed as follows. According to the orbit-stabilizer theorem [21], [the total number of each conformer] is equal to [the order of the rotation group of the coordination geometry] divided by [the order of the rotation group of the conformer], and the sum of the total number of each conformer should be equal to the number of structures (= 3^n for $[MX_{4-n}(AB)_n]$ complex).

The structure of the $[MX_{4-n}(AB)_n]$ complex is defined as shown in Figure 3. In the Cartesian coordinates, the central metal, M, is placed at (0,0,0). The four donor atoms, A (or X), are placed at (*d*, *d*, *d*), (–*d*, –*d*, *d*), (*d*, –*d*, –*d*), and (–*d*, *d*, –*d*) with a positive parameter *d*, and the donor atoms are numbered from 1 to 4 in this order. The M-A distance is expressed as $\sqrt{3}d$. Assuming the bisecting orientation (staggered form), three possible positions for atom, B, are named as *a*, *b*, and *c*, in the clockwise order from the A to M projection. The position of each *a* is on the bisecting plane of the *xz* and *yz* planes. For example, the conformers are expressed as [*a*, *a*, *b*, *c*] for the $[M(AB)_4]$ complex, using the *abc* notation for the positions of B, in the order of the donor atoms from 1 to 4. For the monoatomic X ligand, character "–" is used. For example, [–, *a*, *c*, *b*] for the $[MX(AB)_3]$ complex.

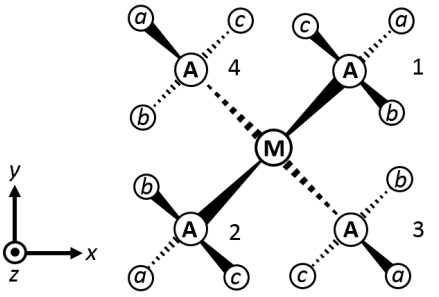

Figure 3. Numbering for the $[M(AB)_4]$ structure. Three possible positions for atom B are indicated by the characters, *a*, *b* and *c*.

3 Results and discussion

3.1 Enumeration for tetrahedral [M(AB)$_4$]

The enumeration of the bisecting conformers was conducted for the tetrahedral [M(AB)$_4$] complex on the basis of the group theory, and the conformers were exhaustively obtained without duplication. The resulting conformers are listed in Table 1, and their structures are depicted in Figure 4. As the result, six conformers, Td4-B1 through Td4-B6, were found [point groups: 1 D_{2d}, 1 S_4, 1 C_2, 1 C_s, and 2 C_1]. Among them, dissymmetric C_2 conformer (Td4-B1) and asymmetric C_1 conformers (Td4-B5 and Td4-B6) are chiral, possessing enantiomers. Except for the C_1 point group, all of the obtained groups are the subgroups of the T_d point group of the tetrahedral MA$_4$ coordination geometry. The completeness of the enumeration can be confirmed by the orbit-stabilizer theorem as follows. For the choice of atom B positions (see Figure 3), there are 3^4 (= 81) structures of the bisecting conformers. The point group of the coordination geometry is T_d, and its order of the rotation group is 12. The order of the rotation groups for the conformers are 4 for D_{2d}, 2 for S_4 and C_2, and 1 for C_s and C_1. Therefore, the total numbers of conformers for the point groups are 3 (= 12/4) for D_{2d}, 6 (= 12/2) for S_4, 6 (= 12/2) for C_2, 12 (= 12/1) for C_s, and 12 (= 12/1) for C_1. Since the C_2 and C_1 structures have their enantiomers, the total number of considered structures is confirmed to be equal to 81 [1 × 3(for D_{2d}) + 1 × 6(for S_4) + 2 × 6(for C_2) + 1 × 12(for C_s) + 2 × 2 × 12(for C_1) = 3 + 6 + 12 + 12 + 48 = 81]. As mentioned in section 1, the edge-orienting conformers can be considered in the same way, and each conformer structure can be obtained by rotating the ligand moieties of the corresponding bisecting conformer by 180° along the M-A bonds.

Table 1. Bisectting conformers for a [M(AB)$_4$] complex.

Code	Example [a]	Point Group
Td4-B1	[*a*, *a*, *a*, *a*]	D_{2d}
Td4-B2	[*b*, *b*, *c*, *c*]	S_4
Td4-B3 [b]	[*a*, *a*, *b*, *b*]	C_2
Td4-B4	[*a*, *a*, *b*, *c*]	C_s
Td4-B5 [b]	[*a*, *a*, *a*, *b*]	C_1
Td4-B6 [b]	[*a*, *c*, *a*, *b*]	C_1

a Order: [(*x*, *y*, *z*) , (–*x*, –*y*, *z*) , (*x*, –*y*, –*z*) , (–*x*, *y*, –*z*)]. *b* Enantiomeric mirror image exists.

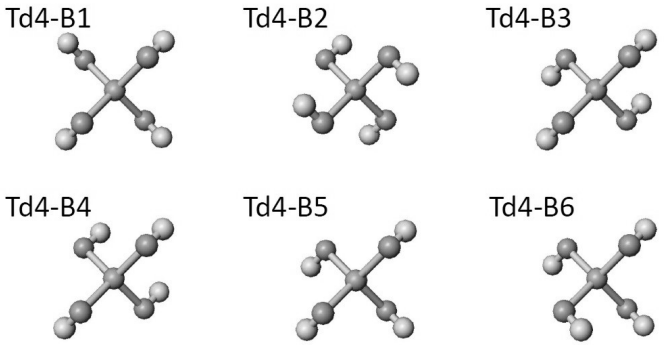

Figure 4. Structures of bisecting conformers for $[M(AB)_4]$ complex, Td4-B1 – Td4-B6.

3.2 Enumeration for tetrahedral $[MX(AB)_3]$

The enumeration of the bisecting conformers was conducted for the tetrahedral $[MX(AB)_3]$ complex on the basis of the group theory, and the conformers were exhaustively obtained without duplication. The resulting conformers are listed in Table 2, and their structures are depicted in Figure 5. As the result, six conformers, Td3-B1 through Td3-B7, were found [point groups: 1 C_{3v}, 1 C_3, 2 C_s, and 3 C_1]. Among them, dissymmetric C_3 conformer (Td3-B2) and asymmetric C_1 conformers (Td3-B5, Td3-B6, and Td3-B7) are chiral, possessing enantiomers. Except for the C_1 point group, all of the obtained groups are the subgroups of the C_{3v} point group of the tetrahedral MXA_3 coordination geometry. The completeness of the enumeration can be confirmed by the orbit-stabilizer theorem as follows. For the choice of atom B positions (see Figure 3), there are 3^3 (= 27) structures of the bisecting conformers. The point group of the coordination geometry is C_{3v}, and its order of the rotation group is 3. The order of the rotation groups for the conformers are 3 for C_{3v} and C_3 and 1 for C_s and C_1. Therefore, the total numbers of conformers for the point groups are 1 (= 3/3) for C_{3v}, 1 (= 3/3) for C_3, 3 (= 3/1) for C_s, and 3 (= 3/1) for C_1. Since the C_3 and C_1 structures have their enantiomers, the total number of considered structures is confirmed to be equal to 27 [1 × 1(for C_{3v}) + 1 × 2 × 1(for C_3) + 2 × 3(for C_s) + 3 × 2 × 3(for C_1) = 1 + 2 + 6 + 18 = 27]. The structures of the edge-orienting conformers can be obtained by rotating the ligand moieties of the corresponding bisecting conformers by 180° along the M-A bonds.

Table 2. Bisectting conformers for a [MX(AB)$_3$] complex.

Code	Example [a]	Point Group
Td3-B1	[–, *a*, *c*, *b*]	C_{3v}
Td3-B2 [b]	[–, *c*, *b*, *a*]	C_3
Td3-B3	[–, *a*, *a*, *a*]	C_s
Td3-B4	[–, *a*, *b*, *c*]	C_s
Td3-B5 [b]	[–, *a*, *a*, *b*]	C_1
Td3-B6 [b]	[–, *b*, *b*, *c*]	C_1
Td3-B7 [b]	[–, *c*, *b*, *b*]	C_1

a Order: [(*x*, *y*, *z*) , (–*x*, –*y*, *z*) , (*x*, –*y*, –*z*) , (–*x*, *y*, –*z*)]. *b* Enantiomeric mirror image exists.

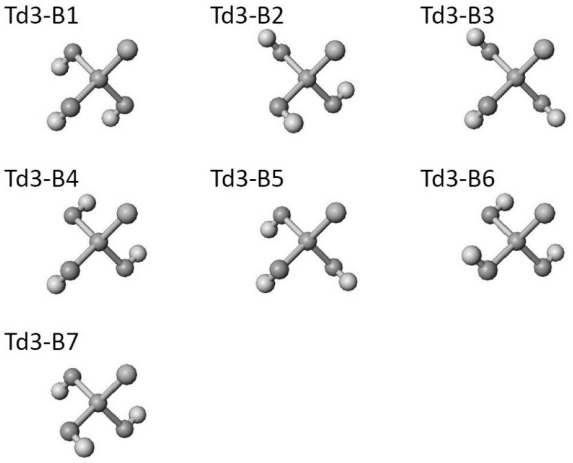

Figure 5. Structures of bisecting conformers for [MX(AB)$_3$] complex, Td3-B1 – Td3-B7.

3.3 Enumeration for tetrahedral [MX$_2$(AB)$_2$]

The enumeration of the bisecting conformers was conducted for the tetrahedral [MX$_2$(AB)$_2$] complex on the basis of the group theory, and the conformers were exhaustively obtained without duplication. The resulting conformers are listed in Table 3, and their structures are depicted in Figure 6. As the result, six conformers, Td2-B1 through Td2-B4, were found [point groups: 1 C_{2v}, 1 C_2, 1 C_s, and 1 C_1]. Among them, dissymmetric C_2 conformer (Td2-B2) and asymmetric C_1 conformer (Td2-B4) are chiral, possessing enantiomers. Except for the C_1 point group, all of the obtained groups are the subgroups of the C_{2v} point group of the tetrahedral MX$_2$A$_2$ coordination geometry. The completeness of the enumeration can be confirmed by the orbit-stabilizer theorem as follows. For the choice of atom B positions (see Figure 3), there are

3^2 (= 9) structures of the bisecting conformers. The point group of the coordination geometry is C_{2v}, and its order of the rotation group is 2. The order of the rotation groups for the conformers are 2 for C_{2v} and C_2 and 1 for C_s and C_1. Therefore, the total numbers of conformers for the point groups are 1 (= 2/2) for C_{2v}, 1 (= 2/2) for C_2, 2 (= 2/1) for C_s, and 2 (= 2/1) for C_1. Since the C_2 and C_1 structures have their enantiomers, the total number of considered structures is confirmed to be equal to 9 [1 × 1(for C_{2v}) + 1 × 2 × 1(for C_2) + 1 × 2(for C_s) + 1 × 2 × 2(for C_1) = 1 + 2 + 2 + 4 = 9]. The structures of the edge-orienting conformers can be obtained by rotating the ligand moieties of the corresponding bisecting conformers by 180° along the M-A bonds.

Table 3. Bisectting conformers for a $[MX_2(AB)_2]$ complex

Code	Example [a]	Point Group
Td2-B1	[*a*, *a*, –, –]	C_{2v}
Td2-B2 [b]	[*b*, *b*, –, –]	C_2
Td2-B3	[*b*, *c*, –, –]	C_s
Td2-B4 [b]	[*a*, *b*, –, –]	C_1

a Order: [(*x*, *y*, *z*) , (–*x*, –*y*, *z*) , (*x*, –*y*, –*z*) , (–*x*, *y*, –*z*)]. *b* Enantiomeric mirror image exists.

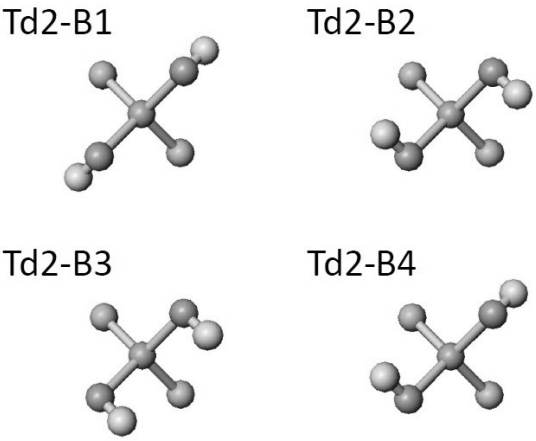

Figure 6. Structures of bisecting conformers for $[MX_2(AB)_2]$ complex, Td2-B1 – Td2-B4.

3.4 Enumeration for tetrahedral [$MX_3(AB)$]

The enumeration of the bisecting conformers was conducted for the tetrahedral [$MX_3(AB)$] complex on the basis of the group theory, and the conformers were exhaustively obtained without duplication. The resulting conformer is listed in Table 4, and its structure is depicted in Figure 7. As the result, one conformer, Td1-B1, was found [point group: 1 C_s]. And the C_s point group is the subgroup of the C_{2v} point group of the tetrahedral MX_2A_2 coordination geometry. The completeness of the enumeration can be confirmed by the orbit-stabilizer theorem as follows. For the choice of atom B positions (see Figure 3), there are 3 structures of the bisecting conformers. The point group of the coordination geometry is C_{3v}, and its order of the rotation group is 3. The order of the rotation group for the conformer is 1 for C_s. Therefore, the total numbers of conformers for the point group is 3 (= 3/1) for C_s, and the total number of considered structures is confirmed to be equal to 3 [1 × 3(for C_s) = 3]. The structures of the edge-orienting conformers can be obtained by rotating the ligand moieties of the corresponding bisecting conformers by 180° along the M-A bonds.

Table 4. Bisectting conformers for a [$MX_3(AB)$] complex

Code	Example [a]	Point Group
Td1-B1	[*a*, –, –, –]	C_s

a Order: [(*x*, *y*, *z*) , (–*x*, –*y*, *z*) , (*x*, –*y*, –*z*) , (–*x*, *y*, –*z*)].

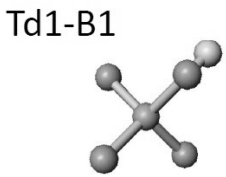

Figure 7. Structure of bisecting conformer for [$MX_4(AB)$] complex, Td1-B1.

4 Concluding remarks

In this study, conformers were enumerated on the basis of group theory method for tetrahedral [$MX_{4-n}(AB)_n$] (n = 1 – 4) complexes as summarized in Tables 1-4. The enumeration result is applicable for various types of rigid monodentate ligands, including dimethylformamide, by

replacing the A and B atoms. The result is expected to be useful in understanding the properties of tetrahedral lithium complexes in electrolyte solutions of lithium-ion batteries.

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