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Enumeration of Conformers of Octahedral [M(ABC)$_6$] Complex on the Basis of Computational Group Theory

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ABSTRACT Conformers of [M(ABC)$_6$] complex have been enumerated on the basis of computational group theory, where M is the central metal, and ABC is the ligand, bound to M through A. Based on the 16 conformers of the M(AB)$_6$ core unit, 7173 conformers have been found for the [M(ABC)$_6$] complex, which are assigned to nine point groups, 1 D_{3d}, 4 D_3, 4 S_6, 5 C_{2h}, 7 C_3, 182 C_2, 15 C_s, 23 C_i, and 6932 C_1.

KEYWORDS Enumeration • conformer • octahedral [M(ABC)$_6$] complex • Computational Group Theory.

1. INTRODUCTION

Group theory is useful in enumerating conformers of a molecule. In the liquid phase or in the gas phase, conformers may coexist in the equilibrium mixed state, and in such a case, it is important to know the structures and ratio of the conformers in order to understand the nature of the compound better. Enumeration by the group theory is mutually exclusive and collectively exhaustive. Therefore, we can efficiently examine the structures of the conformers in conformational analysis.

The conformers of an octahedral [M(AB)$_6$] complex molecule (Figure 1a) have been enumerated [1,2] by the computational group theory (CGT) method [3], where M is the central metal of the molecule, and AB is the ligand including the donor atom, A. Here we say the molecule is "octahedral", because the coordination geometry around the central metal ion, which corresponds to the central MA$_6$ unit, is octahedral. The MA$_6$ unit belongs to O_h point group; however, when M-A-B is bent, the $[M(AB)_6]$ complex molecule can take various structures belonging to D_{3d}, D_3, S_6, C_{2h}, C_3, C_2, C_s, C_i, and C_1 point groups [1], due to the orientation of the ligands. The enumerated conformers were found to be useful in studying actual structures of related metal complexes, e. g. hexakis(methylamine-κ*N*) nickel(II) dication ($[Ni(CH_3NH_2)_6]^{2+}$) and hexakis(*N*-methylformamide-*κO*)nickel(II) dication ($[Ni(NMF)_6]^{2+}$) [1,2].

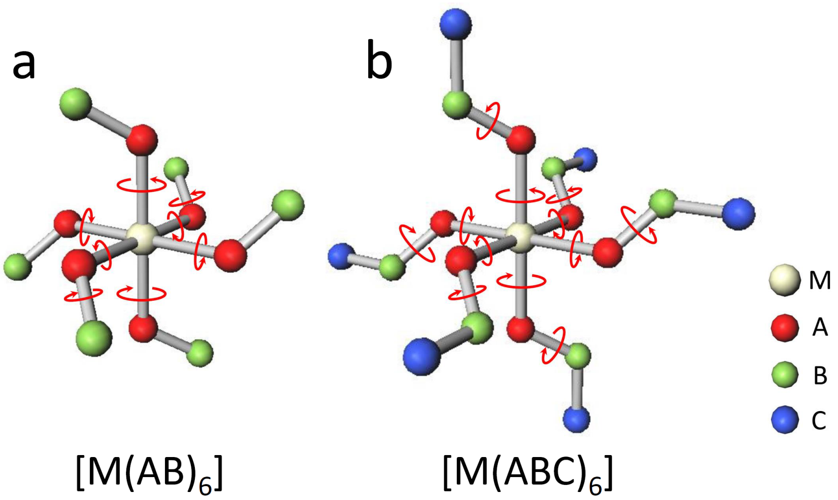

Figure 1. Structures of octahedral metal complexes, $[M(AB)_6]$ (a) and $[M(ABC)_6]$ (b).

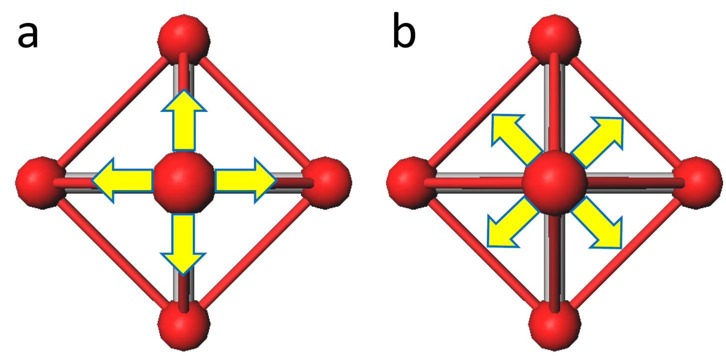

Figure 2. Edge directions (a) and bisected directions (b) from an apex of an octahedron.

Despite the success in enumerating the conformers of $[M(AB)_6]$ complex, the enumeration for the extended $[M(ABC)_6]$ complex (Figure 1b) has not been done. Therefore, in this study, enumeration of the conformers was conducted for $[M(ABC)_6]$ complex by CGT method. The obtained result is expected to be useful in conformational analysis of related metal complexes. When extending the ligand from a donor atom, A, to a bound atom, B, there are two typical directions, edge directions and bisected directions

(Figure 2). In our previous study [2], the edge conformers (meridional conformers) was found to be related with the Fujita's edge configurations of $m = 6$ [4]. In this study, since bisected structures are often seen in actual metal complexes [5,6], only bisected conformers were examined

2. Methods

Conformers were obtained based on the computational group theory (CGT) method [3], which was performed using GAP program [7] on Intel Core i7-3770 (3.40GHz) computer. Three-dimensional models were drawn by Winmostar software [8], and the point groups were ascertained by the software.

3. Results and Discussion

Conformers of $[M(ABC)_6]$ complex were considered based on the previously enumerated conformers of $[M(AB)_6]$ complex. Sixteen bisected conformers of $[M(AB)_6]$ complex are listed in Table 1. Note that we describe, for example, a conformer shown in Figure 3 as [[y+z], [x-z], [x-y], [-y-z], [-x+z], [-x+y]], indicating the orientations of six AB ligands as [y+z], [x-z], etc. in the order of the numbering system [x, y, z, -x, -y, -z]. In this study, based on the $M(AB)_6$ unit, each ligand, AB, was extended from atom B to atom C to consider the conformers of $[M(ABC)_6]$ 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.

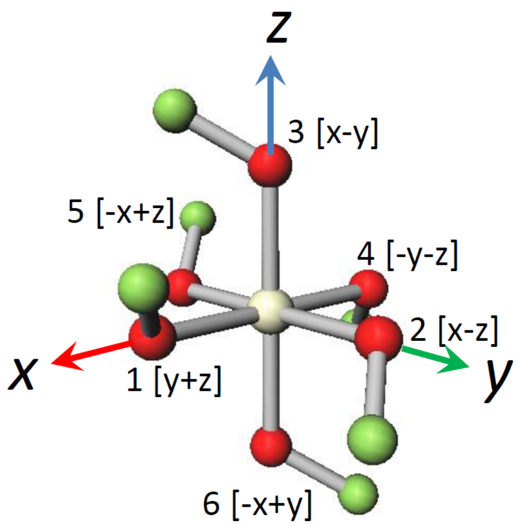

Figure 3. An example of a conformer with a numbering system.

Table 1. Bisected conformers of $[M(AB)_6]$ [1].

No	Example	Point Group
B1	[[y+z], [x-z], [x-y], [-y-z], [-x+z], [-x+y]]	D3d
B2	[[y+z], [-x-z], [x-y], [y+z], [-x-z], [x-y]]	D3
B3	[[y+z], [-x+z], [-x-y], [-y-z], [x-z], [x+y]]	S6
B4	[[y+z], [x-z], [-x+y], [-y-z], [-x+z], [x-y]]	C2h
B5	[[y+z], [-x+z], [x-y], [-y-z], [-x+z], [x-y]]	C2
B6	[[y+z], [-x+z], [x-y], [y-z], [-x+z], [-x-y]]	C2
B7	[[y+z], [x-z], [-x-y], [-y-z], [x+z], [-x+y]]	C2
B8	[[y+z], [-x+z], [-x-y], [-y-z], [x+z], [x-y]]	C2
B9	[[y+z], [-x+z], [x-y], [y-z], [-x-z], [x-y]]	C2
B10	[[y+z], [x-z], [-x+y], [-y-z], [-x+z], [-x+y]]	Cs
B11	[[y+z], [-x-z], [x-y], [-y-z], [-x+z], [x-y]]	C1
B12	[[y+z], [-x+z], [x-y], [y-z], [-x+z], [x-y]]	C1
B13	[[y+z], [-x-z], [-x+y], [-y+z], [-x-z], [x+y]]	C1
B14	[[y+z], [-x+z], [-x-y], [-y-z], [x+z], [-x+y]]	C1
B15	[[y+z], [-x-z], [-x+y], [-y-z], [-x+z], [x-y]]	C1
B16	[[y+z], [-x+z], [x-y], [-y+z], [-x-z], [x+y]]	C1

As the result of CGT computation, for example, in the case of B1 conformer (D_{3d} point group) of the $M(AB)_6$ unit, 74 conformers of $[M(ABC)_6]$ complex, from B1-1 to B1-74, were derived as listed in Table 2. In the list, the conformers were described by dihedral angles (°) of six M-A-B-C units in the order of the numbering system [x, y, z, -x, -y, -z]. The 74 conformers include a D_{3d} structure, a D_3 structure, a S_6 structure, two C_{2h} structures, a C_3 structure, 11 C_2 structures, three C_s structures, three C_i structures, and 51 C_1 structures, and some of the three-dimensional structures are shown in Figure 4. They have different structures; however, their $M(AB)_6$ core units have the same structures, belonging to the D_{3d} point group.

Table 2. Bisected conformers of $[M(ABC)_6]$ possessing $M(AB)_6$ unit of D_{3d} symmetry[a].

No	Dihedral angles (°) of M-A-B-C units	Point Group
B1-1	[180, 180, 180, 180, 180, 180]	D_{3d}
B1-2	[60, 60, 60, 60, 60, 60]	D_3
B1-3	[300, 60, 60, 60, 300, 300]	S_6
B1-4	[180, 300, 60, 180, 60, 300]	C_{2h}
B1-5	[180, 60, 300, 180, 300, 60]	C_{2h}
B1-6	[60, 180, 180, 180, 60, 60]	C_3
B1-7	[180, 60, 180, 180, 60, 180]	C_2
B1-8	[180, 60, 60, 180, 60, 60]	C_2
B1-9	[60, 180, 60, 180, 180, 180]	C_2
B1-10	[60, 300, 60, 180, 300, 180]	C_2
B1-11	[60, 300, 60, 60, 60, 300]	C_2
B1-12	[60, 60, 180, 180, 180, 180]	C_2
B1-13	[60, 60, 300, 180, 180, 300]	C_2
B1-14	[60, 60, 300, 60, 300, 60]	C_2
B1-15	[60, 60, 300, 60, 60, 300]	C_2
B1-16	[60, 60, 60, 180, 180, 60]	C_2
B1-17	[60, 60, 60, 180, 60, 180]	C_2
B1-18	[180, 60, 300, 180, 60, 300]	C_s
B1-19	[60, 180, 180, 180, 180, 300]	C_s
B1-20	[60, 180, 180, 180, 300, 180]	C_s
B1-21	[180, 300, 180, 180, 60, 180]	C_i
B1-22	[180, 300, 300, 180, 60, 60]	C_i
B1-23	[300, 300, 60, 60, 60, 300]	C_i
B1-24	[180, 60, 300, 180, 60, 60]	C_1
B1-25	[180, 60, 60, 180, 60, 300]	C_1
B1-26	[60, 180, 180, 180, 180, 180]	C_1
B1-27	[60, 180, 180, 180, 60, 180]	C_1
B1-28	[60, 180, 180, 180, 60, 300]	C_1
B1-29	[60, 180, 300, 180, 180, 180]	C_1
B1-30	[60, 180, 300, 180, 180, 300]	C_1
B1-31	[60, 180, 300, 180, 180, 60]	C_1
B1-32	[60, 180, 300, 180, 300, 300]	C_1
B1-33	[60, 180, 300, 180, 60, 180]	C_1
B1-34	[60, 180, 300, 180, 60, 300]	C_1
B1-35	[60, 180, 300, 180, 60, 60]	C_1
B1-36	[60, 180, 60, 180, 180, 300]	C_1

B1-37	[60, 180, 60, 180, 180, 60]	C_1
B1-38	[60, 180, 60, 180, 300, 300]	C_1
B1-39	[60, 180, 60, 180, 60, 180]	C_1
B1-40	[60, 180, 60, 180, 60, 300]	C_1
B1-41	[60, 300, 180, 180, 300, 180]	C_1
B1-42	[60, 300, 180, 180, 60, 180]	C_1
B1-43	[60, 300, 180, 180, 60, 300]	C_1
B1-44	[60, 300, 300, 180, 300, 300]	C_1
B1-45	[60, 300, 300, 180, 300, 60]	C_1
B1-46	[60, 300, 300, 180, 60, 180]	C_1
B1-47	[60, 300, 300, 180, 60, 300]	C_1
B1-48	[60, 300, 300, 180, 60, 60]	C_1
B1-49	[60, 300, 300, 60, 60, 300]	C_1
B1-50	[60, 300, 300, 60, 60, 60]	C_1
B1-51	[60, 300, 60, 180, 180, 180]	C_1
B1-52	[60, 300, 60, 180, 180, 300]	C_1
B1-53	[60, 300, 60, 180, 180, 60]	C_1
B1-54	[60, 300, 60, 180, 300, 300]	C_1
B1-55	[60, 300, 60, 180, 300, 60]	C_1
B1-56	[60, 300, 60, 180, 60, 180]	C_1
B1-57	[60, 300, 60, 180, 60, 300]	C_1
B1-58	[60, 300, 60, 180, 60, 60]	C_1
B1-59	[60, 60, 180, 180, 180, 300]	C_1
B1-60	[60, 60, 180, 180, 300, 180]	C_1
B1-61	[60, 60, 180, 180, 60, 180]	C_1
B1-62	[60, 60, 180, 180, 60, 300]	C_1
B1-63	[60, 60, 180, 180, 60, 60]	C_1
B1-64	[60, 60, 300, 180, 300, 300]	C_1
B1-65	[60, 60, 300, 180, 300, 60]	C_1
B1-66	[60, 60, 300, 180, 60, 180]	C_1
B1-67	[60, 60, 300, 180, 60, 300]	C_1
B1-68	[60, 60, 300, 180, 60, 60]	C_1
B1-69	[60, 60, 60, 180, 180, 300]	C_1
B1-70	[60, 60, 60, 180, 300, 300]	C_1
B1-71	[60, 60, 60, 180, 300, 60]	C_1
B1-72	[60, 60, 60, 180, 60, 300]	C_1
B1-73	[60, 60, 60, 180, 60, 60]	C_1
B1-74	[60, 60, 60, 60, 60, 300]	C_1

[a] The orientation is [[y+z], [x-z], [x-y], [-y-z], [-x+z], [-x+y]].

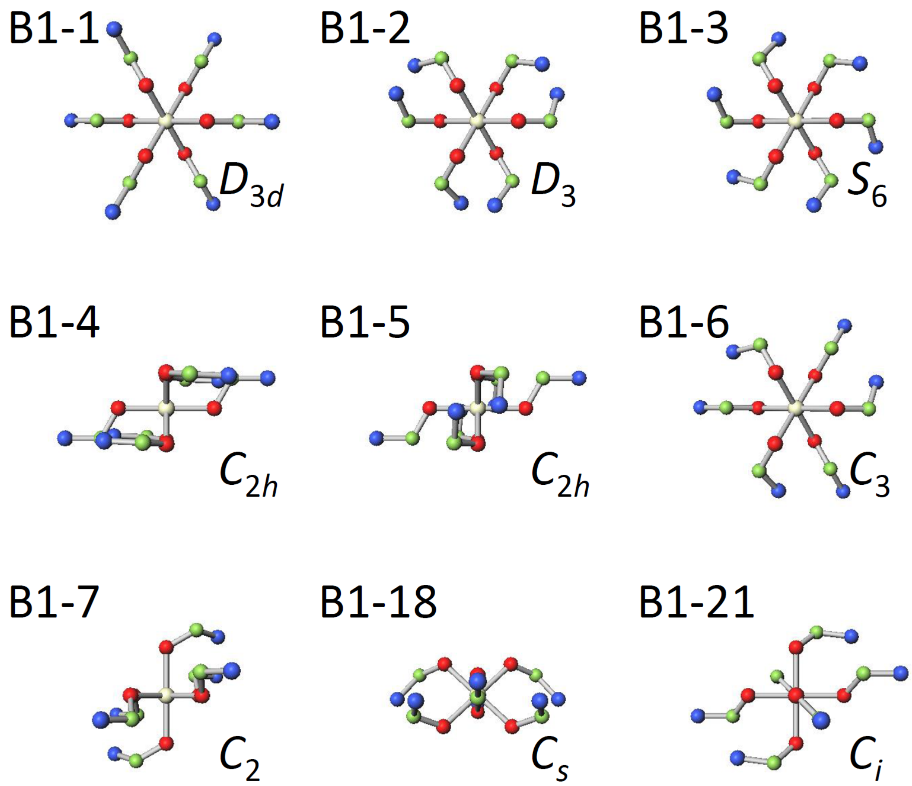

Figure 4. Examples of conformers for $[M(ABC)_6]$ possessing $M(AB)_6$ unit of D_{3d} symmetry.

In the same way, the rest of the conformers of the $[M(ABC)_6]$ complex were considered based on the $M(AB)_6$ core units from B2 to B16, and the point groups of the obtained conformers are summarized in Table 3. In total, 7173 conformers were found as the bisected conformers of $[M(ABC)_6]$ complex. In Table 4, the 7173 conformers were re-categorized based on the resulting nine point groups, D_{3d}, D_3, S_6, C_{2h}, C_3, C_2, C_s, C_i, and C_1. Except for the C_1 symmetry, all of the other 241 bisected conformers of $[M(ABC)_6]$ are tabled in Table S5 in supporting information. Some of the structures are depicted in Figure 5.

Table 2. Bisected conformers of [M(ABC)$_6$] possessing M(AB)$_6$ unit of D_{3d} symmetry[a].

No	Dihedral angles (°) of M-A-B-C units	Point Group
B1-1	[180, 180, 180, 180, 180, 180]	D_{3d}
B1-2	[60, 60, 60, 60, 60, 60]	D_3
B1-3	[300, 60, 60, 60, 300, 300]	S_6
B1-4	[180, 300, 60, 180, 60, 300]	C_{2h}
B1-5	[180, 60, 300, 180, 300, 60]	C_{2h}
B1-6	[60, 180, 180, 180, 60, 60]	C_3
B1-7	[180, 60, 180, 180, 60, 180]	C_2
B1-8	[180, 60, 60, 180, 60, 60]	C_2
B1-9	[60, 180, 60, 180, 180, 180]	C_2
B1-10	[60, 300, 60, 180, 300, 180]	C_2
B1-11	[60, 300, 60, 60, 60, 300]	C_2
B1-12	[60, 60, 180, 180, 180, 180]	C_2
B1-13	[60, 60, 300, 180, 180, 300]	C_2
B1-14	[60, 60, 300, 60, 300, 60]	C_2
B1-15	[60, 60, 300, 60, 60, 300]	C_2
B1-16	[60, 60, 60, 180, 180, 60]	C_2
B1-17	[60, 60, 60, 180, 60, 180]	C_2
B1-18	[180, 60, 300, 180, 60, 300]	C_s
B1-19	[60, 180, 180, 180, 180, 300]	C_s
B1-20	[60, 180, 180, 180, 300, 180]	C_s
B1-21	[180, 300, 180, 180, 60, 180]	C_i
B1-22	[180, 300, 300, 180, 60, 60]	C_i
B1-23	[300, 300, 60, 60, 60, 300]	C_i
B1-24	[180, 60, 300, 180, 60, 60]	C_1
B1-25	[180, 60, 60, 180, 60, 300]	C_1
B1-26	[60, 180, 180, 180, 180, 180]	C_1
B1-27	[60, 180, 180, 180, 60, 180]	C_1
B1-28	[60, 180, 180, 180, 60, 300]	C_1
B1-29	[60, 180, 300, 180, 180, 180]	C_1
B1-30	[60, 180, 300, 180, 180, 300]	C_1
B1-31	[60, 180, 300, 180, 180, 60]	C_1
B1-32	[60, 180, 300, 180, 300, 300]	C_1
B1-33	[60, 180, 300, 180, 60, 180]	C_1
B1-34	[60, 180, 300, 180, 60, 300]	C_1
B1-35	[60, 180, 300, 180, 60, 60]	C_1
B1-36	[60, 180, 60, 180, 180, 300]	C_1

B1-37	[60, 180, 60, 180, 180, 60]	C_1
B1-38	[60, 180, 60, 180, 300, 300]	C_1
B1-39	[60, 180, 60, 180, 60, 180]	C_1
B1-40	[60, 180, 60, 180, 60, 300]	C_1
B1-41	[60, 300, 180, 180, 300, 180]	C_1
B1-42	[60, 300, 180, 180, 60, 180]	C_1
B1-43	[60, 300, 180, 180, 60, 300]	C_1
B1-44	[60, 300, 300, 180, 300, 300]	C_1
B1-45	[60, 300, 300, 180, 300, 60]	C_1
B1-46	[60, 300, 300, 180, 60, 180]	C_1
B1-47	[60, 300, 300, 180, 60, 300]	C_1
B1-48	[60, 300, 300, 180, 60, 60]	C_1
B1-49	[60, 300, 300, 60, 60, 300]	C_1
B1-50	[60, 300, 300, 60, 60, 60]	C_1
B1-51	[60, 300, 60, 180, 180, 180]	C_1
B1-52	[60, 300, 60, 180, 180, 300]	C_1
B1-53	[60, 300, 60, 180, 180, 60]	C_1
B1-54	[60, 300, 60, 180, 300, 300]	C_1
B1-55	[60, 300, 60, 180, 300, 60]	C_1
B1-56	[60, 300, 60, 180, 60, 180]	C_1
B1-57	[60, 300, 60, 180, 60, 300]	C_1
B1-58	[60, 300, 60, 180, 60, 60]	C_1
B1-59	[60, 60, 180, 180, 180, 300]	C_1
B1-60	[60, 60, 180, 180, 300, 180]	C_1
B1-61	[60, 60, 180, 180, 60, 180]	C_1
B1-62	[60, 60, 180, 180, 60, 300]	C_1
B1-63	[60, 60, 180, 180, 60, 60]	C_1
B1-64	[60, 60, 300, 180, 300, 300]	C_1
B1-65	[60, 60, 300, 180, 300, 60]	C_1
B1-66	[60, 60, 300, 180, 60, 180]	C_1
B1-67	[60, 60, 300, 180, 60, 300]	C_1
B1-68	[60, 60, 300, 180, 60, 60]	C_1
B1-69	[60, 60, 60, 180, 180, 300]	C_1
B1-70	[60, 60, 60, 180, 300, 300]	C_1
B1-71	[60, 60, 60, 180, 300, 60]	C_1
B1-72	[60, 60, 60, 180, 60, 300]	C_1
B1-73	[60, 60, 60, 180, 60, 60]	C_1
B1-74	[60, 60, 60, 60, 60, 300]	C_1

[a] The orientation is [[y+z], [x-z], [x-y], [-y-z], [-x+z], [-x+y]].

Table 3. Conformers of [M(ABC)$_6$] derived from M(AB)$_6$ core unit.

No	Point Group of M(AB)$_6$ Core Unit	Point Groups of [M(ABC)$_6$] Conformer	Total
B1	D_{3d}	D_{3d}, D_3, S_6, 2 C_{2h}, C_3, 11 C_2, 3 C_s, 3 C_i, 51 C_1	74
B2	D_3	3 D_3, 3 C_3, 24 C_2, 108 C_1	138
B3	S_6	3 S_6, 3 C_3, 8 C_i, 116 C_1	130
B4	C_{2h}	3 C_{2h}, 12 C_2, 3 C_s, 12 C_i, 168 C_1	198
B5	C_2	27 C_2, 351 C_1	378
B6	C_2	27 C_2, 351 C_1	378
B7	C_2	27 C_2, 351 C_1	378
B8	C_2	27 C_2, 351 C_1	378
B9	C_2	27 C_2, 351 C_1	378
B10	C_s	9 C_s, 360 C_1	369
B11	C_1	729 C_1	729
B12	C_1	729 C_1	729
B13	C_1	729 C_1	729
B14	C_1	729 C_1	729
B15	C_1	729 C_1	729
B16	C_1	729 C_1	729
		Total	7173

Table 4. Conformers of [M(ABC)$_6$].

No	Point Group of [M(ABC)$_6$] Conformer	Total
1	D_{3d}	1
2	D_3	4
3	S_6	4
4	C_{2h}	5
5	C_3	7
6	C_2	182
7	C_s	15
8	C_i	23
9	C_1	6932
	Total	7173

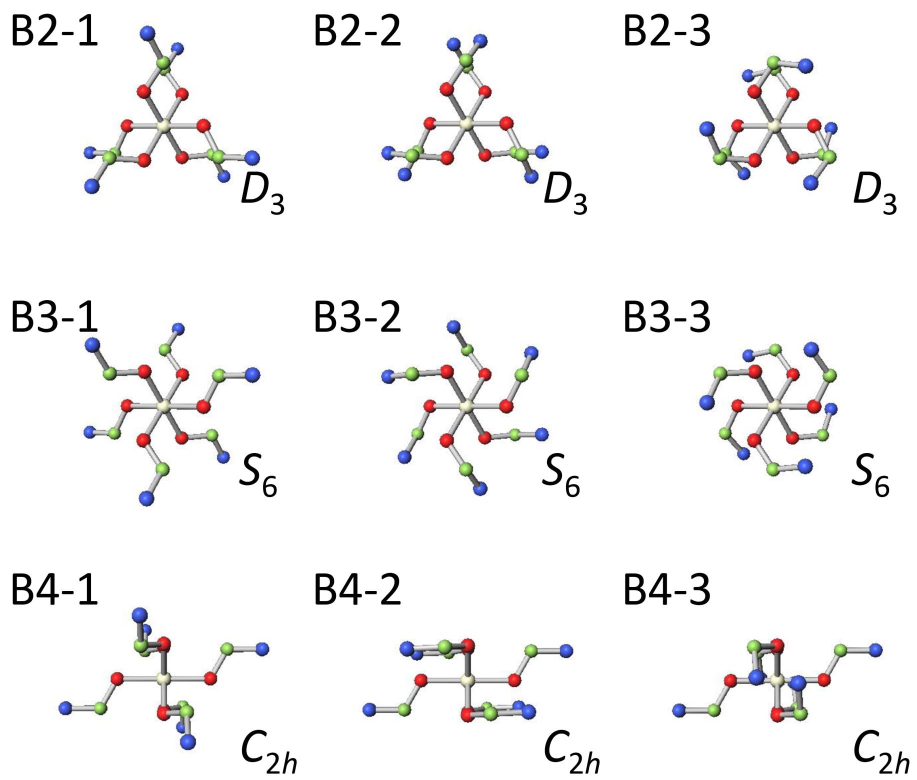

Figure 5. Examples of conformers for $[M(ABC)_6]$.

4. CONCLUDING REMARKS

In this study, conformers of octahedral $[M(ABC)_6]$ complex have been enumerated on the basis of computational group theory. Based on the 16 bisected conformers of the $M(AB)_6$ core unit, 7173 conformers have been found for the $[M(ABC)_6]$ complex, considering the anti and gauche conformations. The obtained structures were assigned to nine point groups, 1 D_{3d}, 4 D_3, 4 S_6, 5 C_{2h}, 7 C_3, 182 C_2, 15 C_s, 23 C_i, and 6932 C_1. The results were summarized in tables, which is useful in conformational analysis of the related octahedral complexes.

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SUPPORTING INFORMATION: Table S5.

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