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Enumeration of Conformers for Octahedral $[M(AB_2)_6]$ Complexes and Conformational Prediction for a Related Metal Complex

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Abstract

Conformers of octahedral $[M(AB_2)_6]$ complex have been enumerated on the basis of computational group theory, where M and AB_2 are the central metal atom and the symmetrical triatomic ligand with a donor atom A, respectively. In the complex, each MAB_2 unit is assumed to belong to the local C_{2v} point group; all of the four atoms in the local unit are on the same plane, the A-B distances are the same, and the M-A-B angles are the same. For the edge-orienting case, seven conformers – belonging to the T_h, D_3, D_{2h}, D_{2d}, D_{2d}, C_{2v}, and C_s point groups – were obtained. For the bisecting case, seven conformers – belonging to the T_d, D_{3d}, D_{3d}, D_{2d}, D_2, C_{2v}, and C_s point groups – were obtained. The enumeration result is expected to be useful in conformational analysis of related metal complexes, including hexakis-pyridine (py) complexes. On the basis of the density functional theory (DFT) calculation for the $[Mg(py)_6]^{2+}$ complex cation, the edge-orienting T_h conformer was found to be the only stable conformer. That is, other conformers are not suitable due to the inter-ligand steric repulsion. On the other hand, the structure of the edge-orienting T_h conformer is somewhat stabilized by the inter-ligand CH···π interactions. This conformational prediction is consistent with the crystallographically identified structure of $[Fe(py)_6]^{2+}$ complex cation.

1 Introduction

Enumerating conformers of metal complexes is very helpful for conformational prediction of flexible metal complexes, and fundamental enumerations have been actively investigated for cubic symmetry [1–7]. Systematic enumeration has been conducted for octahedral metal complexes with AB type and bent ABC type ligands (Figure 1), which coordinate to metal ions through A in bent forms [8–13]. Using the enumeration results, conformational predictions were successfully conducted for some metal complexes. For example, the crystal structures of hexakis-dimethylsulfoxide (dmso) magnesium complexes ($[Mg(dmso)_6]^{2+}$ complexes [14,15]) and pentakis-dmso oxidovanadium(IV) complex ($[VO(dmso)_5]^{2+}$ complex [16]) were successfully reproduced [15,16], using the enumeration results for octahedral $[M(ABC)_6]$ and $[MX(ABC)_5]$ complexes [8,9], respectively, where M, ABC, and X are a metal atom, triatomic ligand, and monoatomic ligand, respectively.

Enumeration of the conformers for octahedral metal complexes were previously conducted only for the AB and bent ABC type ligands, and these are not sufficient for C_{2v}-symmetric ligands, *e.g.* pyridine (py) ligand. Therefore, in this study, conformer enumeration was conducted for octahedral metal complex with six C_{2v}-symmetric AB_2 ligand (Figure 1c), $[M(AB_2)_6]$. Furthermore, conformational prediction was conducted for the related $[Mg(AB_2)_6]^{2+}$ complex cation.

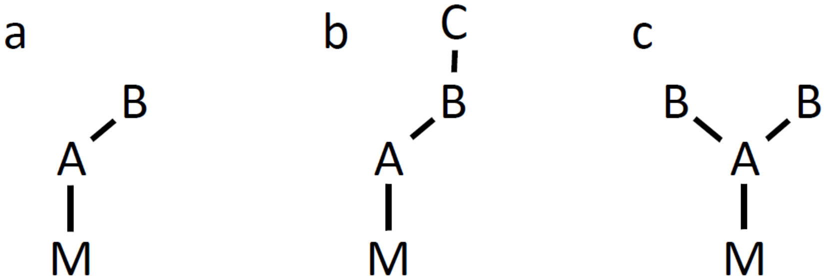

Figure 1. Three typical ligand moieties: an AB ligand in a bent form (a), a bent ABC ligand in a bent form (b), and a symmetrical AB_2 ligand (c).

2 Methods

Conformers were obtained based on the computational group theory (CGT) method [17], which was performed using GAP program [18]. Three-dimensional models were handled by Winmostar software [19], and the point groups were confirmed by the software. Density functional theory (DFT) computations were performed using GAMESS program [20,21] on Fujitsu PRIMERGY CX2550/CX2560 M4 (ITO super computer system) at Kyushu University. Structural optimizations were performed with LC-BOP/6-31G [22].

3 Results and discussion

3.1 Enumeration for octahedral [M(AB_2)$_6$] complexes

In considering the conformers for octahedral [M(AB_2)$_6$] complex, only typical orientations of the B atoms, edge and bisecting orientations, were taken into account. In the edge orientation, the ABB plain is on the edge of the octahedral coordination geometry, while in the bisecting orientation, the ABB plain is in the bisecting direction between the edges of the octahedral geometry (Figure 2). The enumeration was conducted for the [M(AB_2)$_6$] complex on the basis of the group theory. In total, 2^6 (= 64) structures can be considered for each case of the edge and bisecting orientations. Each of the 64 structures was subjected to all rotation operations of the cubic group and the resulting different structures and their stabilizer subgroups were obtained in the enumeration process. The enumeration algorithm is described in reference 17. The conformers were exhaustively obtained without duplication, and the resulting conformers are listed in Tables 1 and 2, and their structures are depicted in Figures 3 and 4. For the edge-orienting conformers, seven conformers, P6-A1 through P6-A7, were found to be possible. Their point groups are T_h, D_3, D_{2h}, D_{2d}, D_{2d}, C_{2v}, and C_s, which are all subgroups of the O_h point group, although not all the subgroups are included due to the steric requirement. The D_{2d} point group appeared twice, but they are different structures. For the bisecting conformers, seven conformers, P6-B1 through P6-B7, were found to be possible, and their point groups are T_d, D_{3d}, D_{3d}, D_{2d}, D_2, C_{2v}, and C_s. Again, they are all subgroups of the O_h point group, but not all the subgroups are included due to the steric requirement. The two conformers belonging to the

D_{3d} point group are different structures. In all of the obtained conformers, the D_3 and D_2 conformers are chiral.

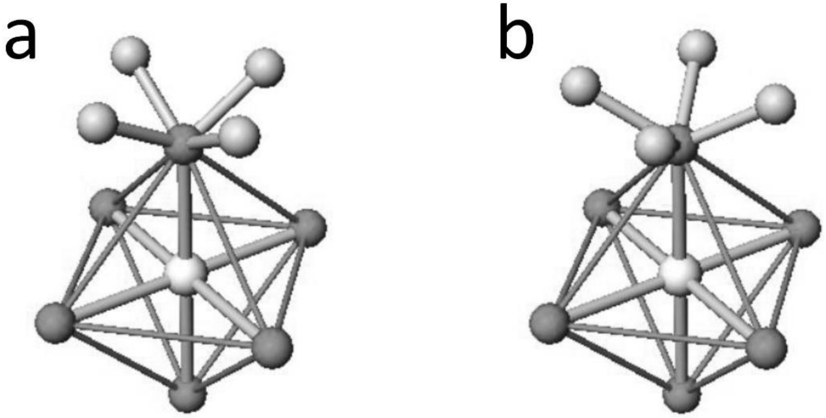

Figure 2. Typical orientations with respect to the octahedral coordination geometry: edge orientations (a) and bisecting orientations (b).

Table 1. Edge-orienting conformers for a [M(AB_2)$_6$] complex

Code	Example [a]	Point Group
P6-A1	[[$\pm y$], [$\pm z$], [$\pm x$], [$\pm y$], [$\pm z$], [$\pm x$]]	T_h
P6-A2 [b]	[[$\pm z$], [$\pm z$], [$\pm y$], [$\pm y$], [$\pm x$], [$\pm x$]]	D_3
P6-A3	[[$\pm y$], [$\pm x$], [$\pm x$], [$\pm y$], [$\pm x$], [$\pm x$]]	D_{2h}
P6-A4	[[$\pm z$], [$\pm x$], [$\pm x$], [$\pm y$], [$\pm x$], [$\pm x$]]	D_{2d}
P6-A5	[[$\pm y$], [$\pm x$], [$\pm y$], [$\pm y$], [$\pm x$], [$\pm x$]]	D_{2d}
P6-A6	[[$\pm y$], [$\pm z$], [$\pm x$], [$\pm y$], [$\pm x$], [$\pm x$]]	C_{2v}
P6-A7	[[$\pm z$], [$\pm z$], [$\pm x$], [$\pm y$], [$\pm x$], [$\pm x$]]	C_s

a Order: (x, y, z, $-x$, $-y$, $-z$). *b* Enantiomeric mirror image exists.

Table 2. Bisecting conformers for a $[M(AB_2)_6]$ complex

Code	Example [a]	Point Group
P6-B1	$[\,[\pm y \pm z], [\pm x \pm z], [\pm x \pm y], [\pm y \mp z], [\pm x \mp z], [\pm x \mp y]\,]$	T_d
P6-B2	$[\,[\pm y \mp z], [\pm x \mp z], [\pm x \mp y], [\pm y \mp z], [\pm x \mp z], [\pm x \mp y]\,]$	D_{3d}
P6-B3	$[\,[\pm y \mp z], [\pm x \mp z], [\pm x \pm y], [\pm y \mp z], [\pm x \mp z], [\pm x \pm y]\,]$	D_{3d}
P6-B4	$[\,[\pm y \pm z], [\pm x \pm z], [\pm x \mp y], [\pm y \mp z], [\pm x \mp z], [\pm x \pm y]\,]$	D_{2d}
P6-B5 [b]	$[\,[\pm y \pm z], [\pm x \mp z], [\pm x \mp y], [\pm y \mp z], [\pm x \mp z], [\pm x \pm y]\,]$	D_2
P6-B6	$[\,[\pm y \pm z], [\pm x \pm z], [\pm x \mp y], [\pm y \mp z], [\pm x \mp z], [\pm x \mp y]\,]$	C_{2v}
P6-B7	$[\,[\pm y \pm z], [\pm x \mp z], [\pm x \mp y], [\pm y \mp z], [\pm x \mp z], [\pm x \mp y]\,]$	C_s

a Order: $(x, y, z, -x, -y, -z)$. *b* Enantiomeric mirror image exists.

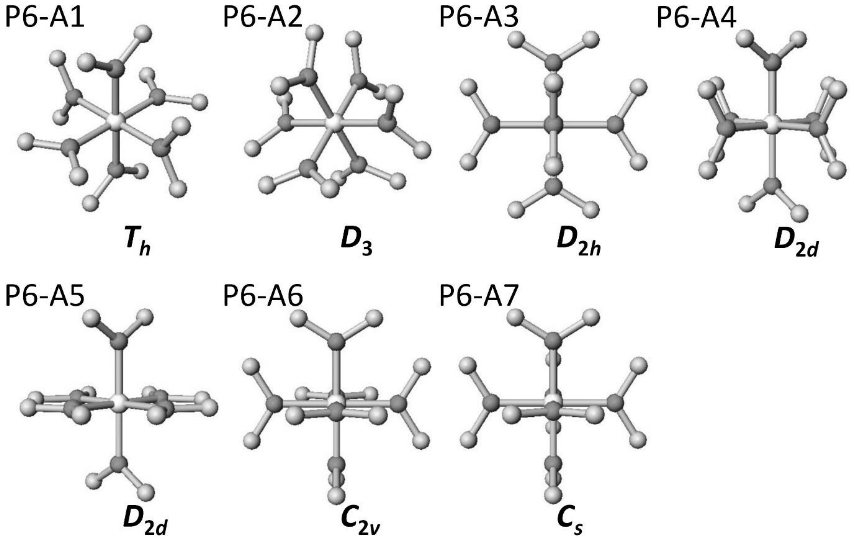

Figure 3. Structures of edge-orienting conformers for $[M(AB_2)_6]$ complex, P6-A1 – P6-A7.

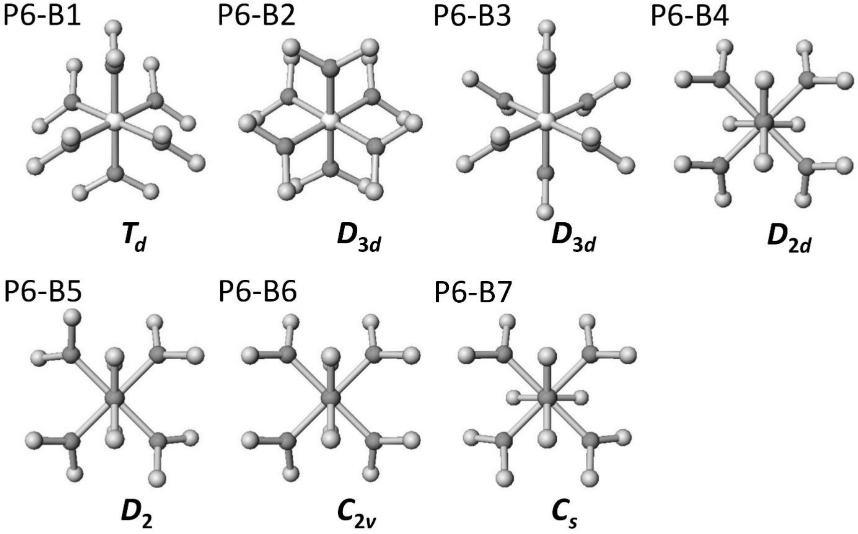

Figure 4. Structures of bisecting conformers for [M(AB_2)$_6$] complex, P6-B1 – P6-B7.

The completeness of each enumeration can be confirmed according to the orbit-stabilizer theorem in reference 17 as follows. The order of the cubic rotation group is 24. According to the theorem, the product of [the total number of structures in the 2^6 (= 64) structures] and [the order of the stabilizer subgroup] is equal to 24. For each conformer structure, the total number of conformer structures are confirmed by the theorem, and the sum of each number of conformer structures is confirmed to be 64.

3.2 Conformational prediction for [Mg(py)$_6$]$^{2+}$ complex cation

The enumeration results are expected to be useful for conformational analysis and conformational prediction for related metal complexes. For the purpose of demonstration, the conformational prediction was conducted for an ideal hexakis-pyridine magnesium complex cation, [Mg(py)$_6$]$^{2+}$, using the enumeration result. In the initial structure, the Mg-N bond lengths were set to 2.10 Å. The six edge-orienting conformers, P6-A2 – P6-A7, were found to be impossible due to the inter-ligand steric hindrance. After structure optimization by the DFT method, the structure of conformer P6-B1 was broken due to the inter-ligand steric repulsion, but the structures of the remaining seven conformers were successfully optimized as summarized in Table 3. The resulting seven structures are shown in Figure 5. The most stable structure was found to be conformer P6-A1, belonging to the T_h point group. Judging from the energy difference between the most and the second most stable conformers (2.6 kcal mol^{-1}), which is larger than the thermal energy value (kT = 0.60 kcal mol^{-1} at 300 K), the T_h conformer is considered to be the only species for the $[Mg(py)_6]^{2+}$ complex cation. Judging from the structures, other conformers are not suitable due to the inter-ligand steric repulsion. In the most stable structure, the inter-ligand neighboring C···H and N···H distances are 2.83 and 2.42 Å, respectively. Since these distances are slightly shorter than the sum of van der Waals radii (2.79-2.90 and 2.64-2.75 Å, respectively), this structure is suitable for the CH···π interactions. Earlier, the influence of the *d*-orbital occupancy was thoroughly investigated on the basis of DFT methods [23]. The crystal structure of hexakis-pyridine metal complex has rarely been reported [24,25]; however, in the crystal of $[Fe(py)_6][Fe_4(CO)_{13}]$, the symmetry of $[Fe(py)_6]^{2+}$ was found to belong to the T_h symmetry [26], which is consistent with the prediction in this study.

Table 3. Energy difference between conformers of $[Mg(py)_6]^{2+}$ complex cation.

Code	Point group before optimization	Point group after optimization	ΔE(kcal mol^{-1})
P6-A1	T_h	T_h	0.0
P6-B5	D_2	D_2	2.6
P6-B4	D_{2d}	D_{2d}	4.4
P6-B3	D_{3d}	D_{3d} (1)	8.2
P6-B7	C_s	C_s	14.8
P6-B6	C_{2v}	*pseudo*-C_{2v}	22.5
P6-B2	D_{3d}	D_{3d} (2)	27.6

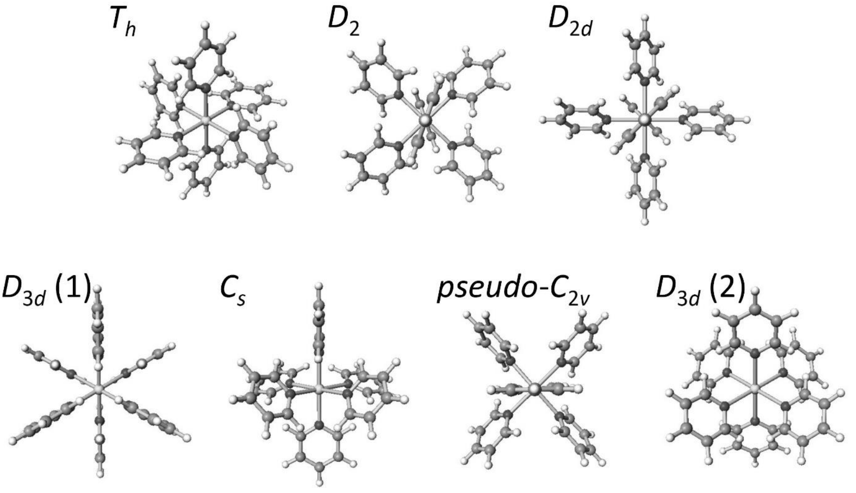

Figure 5. Structures of optimized conformers for $[Mg(py)_6]^{2+}$ complex cation.

4 Concluding remarks

In this study, conformers of octahedral $[M(AB_2)_6]$ complex were enumerated on the basis of computational group theory. As the edge-orienting conformers, seven conformers, belonging to the T_h, D_3, D_{2h}, D_{2d}, D_{2d}, C_{2v}, and C_s point groups, were obtained. As the bisecting conformers, seven conformers, belonging to the T_d, D_{3d}, D_{3d}, D_{2d}, D_2, C_{2v}, and C_s point groups, were obtained. Using the enumeration result, the structure optimization was conducted for $[Mg(py)_6]^{2+}$ complex cation, and only the T_h conformer was found to be possible; other conformers were found to be not suitable due to the inter-ligand steric repulsion. The T_h conformer was also found to be suitable for inter-ligand CH$\cdots\pi$ interaction. The conformational prediction in this study is consistent with the cystallographically identified structure of $[Fe(py)_6]^{2+}$ complex cation of the T_h symmetry.

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