General Paper

Conformational Analysis of Hexakis-*N*-Methylformamide Nickel(II) Complex on the Basis of Computational Group Theory and Density Functional Theory

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Conformational analysis was conducted for a hexakis-*N*-methylformamide nickel(II) complex cation, $[\text{Ni}(\text{NMF})_6]^{2+}$ [hexakis(*N*-methylformamide- κO)nickel(II) dication], by the semi-empirical PM6 method and the Density Functional Theory (DFT) method, using 54 possible conformers obtained by the Computational Group Theory (CGT) method as initial structures. In the preliminary structural optimization by the PM6, all of the initial structures converted to only two conformers, *pseudo-S*₆ and *pseudo-D*₃ conformers. Subsequently, the structures of the two conformers were optimized by the DFT method, and the *pseudo-S*₆ conformer was found to be more stable than the *pseudo-D*₃ conformer by 1.8 ~ 2.2 kcal mol⁻¹. From the energy difference, the *pseudo-S*₆ conformer was found to be practically the only species at room temperature. This result is consistent with the crystal structure.

Keywords: Conformational analysis, Hexakis-*N*-methylformamide complex, Nickel(II) complex, Computational group theory (CGT) method, Density Functional Theory (DFT) method

1 INTRODUCTION

When six monodentate ligands bind to a metal ion in bent forms (**Figure 1**), how many conformational isomers exist for the octahedral metal complex? It is worth answering this question when the structure cannot be determined experimentally and we need to determine the structure computationally. That is because any molecular computations require initial structures, and we should consider all the possibilities in order not to make mistakes.

It is not easy to find all the possible structures [1–4]; however, we previously investigated [5] all the possible isomers of a hexakis-methylamine nickel(II) complex cation $[\text{Ni}(\text{CH}_3\text{NH}_2)_6]^{2+}$ [hexakis-(methylamine- κN)nickel(II) dication] by computational group theory (CGT) method [6]. We showed there are 36 meridional diastereomers and 16 bisected diastereomers, where the meridional diastereomers have six methylamine ligands on the edges of the N_6 octahedron around the nickel(II) ion, and the bisected diastereomers have their six ligands bisecting the edges. Both groups of diastereomers are mutually exclusive and collectively exhaustive. A relationship between the 36 meridional diastereomers and the 30 edge configurations for $m = 6$ [7] is as follows: if we consider putting six arrows from each apex of an octahedron, the 30 edge

configurations are reduced to 23 configurations (**Table 1**); considering the directions of arrows subsequently, the number of real arrow edge configurations becomes 38. The corresponding point groups of the real arrow edge configurations are also summarized in **Table 1**.

We also previously investigated the isomers of $[\text{Ni}(\text{DMF})_6]^{2+}$ (DMF = *N,N*-dimethylformamide) [3]; however, we eliminated unfavorable structures empirically to reduce the number of possible isomers. Therefore, in the present study, in order not to rely on the empirical elimination method, we investigated isomers of a related hexakis-*N*-methylformamide nickel(II) complex cation,

Figure 1. An octahedral complex with six ligands in bent forms.

Table 1. Number of configurations of edge configurations and arrow edge configurations

Symmetry	Number of edge configurations ($m = 6$) [7]	Number of possible edge configurations for arrow edge configurations	Number of real arrow edge configurations
C_1	14	12	$24C_1$
C_2'	2	2	$C_1, 2C_2$
C_s	2	1	C_1
C_s'	2	1	C_1'
C_3	1	1	$2C_3$
D_2'	1	1	C_2
C_{2v}	2	1	C_s
C_{2v}'	1	0	–
C_{2v}''	2	1	C_2
C_{2h}	1	1	C_i
D_{3d}	2	2	$2S_6, D_3$
Sum	30	23	38

$[\text{Ni}(\text{NMF})_6]^{2+}$ [hexakis(*N*-methylformamide- κO)nickel(II) dication] (NMF = *N*-methylformamide), using CGT method.

2 METHODS

2.1 Finding initial conformers

All the possible conformers were obtained using previous tables (Tables 2 and 3) [5] obtained by the CGT method [6]. Computational molecular structures were constructed using Winmostar software [8].

2.2 Structural optimization

All of the initial conformers were optimized using MOPAC2012 [9] program based on the semi-empirical PM6 method [10], and the resulting conformers were optimized based on the Density Functional Theory (DFT) method computation. DFT computations were performed using GAMESS program [11,12] on FUJITSU PRIMERGY CX400 (TATARA computer) at Kyushu University. Structural optimizations were performed with LC-BOP/6-31G, LC-BOP/6-31G*, LC-BOP/6-31G**, LC-BLYP/6-31G, LC-BLYP/6-31G*, and LC-BLYP/6-31G** [13]. Molecular structures were drawn using Winmostar software [8].

3 RESULTS AND DISCUSSION

3.1 Finding initial conformers for hexakis-*N*-methylformamide nickel(II) complex cation

All of the possible initial structures for the hexakis-*N*-methylformamide nickel(II) complex cation, $[\text{Ni}(\text{NMF})_6]^{2+}$, were obtained based on the previous tables (Tables 2 and 3). Note that we describe, for example, a conformer shown in Figure 2B as [y], [-z], [-y], [z], [-x], [x]; meridional planes are described as [y], [-z], and so on; bisected planes are described as [y+z], [x-z], and so on.

Table 2. Meridional diastereomers [5]

No	Example	Point Group
A1	[[y], [-z], [-y], [z], [-x], [x]]	D_3
A2	[[y], [z], [-x], [y], [z], [-x]]	C_3
A3	[[y], [-x], [-x], [-z], [-z], [y]]	C_3
A4	[[y], [z], [x], [-y], [-z], [-x]]	S_6
A5	[[y], [-z], [x], [-y], [z], [-x]]	S_6
A6	[[y], [-x], [x], [-z], [-x], [x]]	C_2
A7	[[y], [-z], [y], [z], [-x], [-x]]	C_2
A8	[[y], [-x], [-y], [-y], [-z], [y]]	C_2
A9	[[y], [z], [-y], [-z], [-x], [x]]	C_2
A10	[[y], [-x], [x], [-y], [x], [-x]]	C_i
A11	[[y], [-x], [y], [-z], [-x], [y]]	C_1
A12	[[y], [-x], [-x], [-z], [-x], [y]]	C_1
A13	[[y], [-x], [y], [-z], [z], [y]]	C_1
A14	[[y], [-x], [-x], [-y], [-z], [-x]]	C_1
A15	[[y], [-x], [y], [-y], [-z], [y]]	C_1
A16	[[y], [-x], [-x], [-y], [x], [-x]]	C_s
A17	[[y], [-x], [-y], [z], [-x], [-y]]	C_1
A18	[[y], [-z], [-x], [-y], [-z], [-x]]	C_1
A19	[[y], [-z], [-y], [-y], [-z], [-x]]	C_1
A20	[[y], [-z], [y], [-y], [-z], [-x]]	C_1
A21	[[y], [z], [-x], [-y], [-z], [-x]]	C_1
A22	[[y], [-x], [x], [-z], [-x], [y]]	C_1
A23	[[y], [-x], [-y], [z], [-x], [x]]	C_1
A24	[[y], [-x], [y], [-z], [-x], [x]]	C_1
A25	[[y], [z], [-x], [-z], [z], [-y]]	C_1
A26	[[y], [-z], [-x], [-y], [x], [-x]]	C_1
A27	[[y], [-z], [y], [-z], [-x], [x]]	C_1
A28	[[y], [-x], [-y], [-y], [-z], [-x]]	C_1
A29	[[y], [-z], [-y], [-z], [-x], [x]]	C_1
A30	[[y], [-x], [y], [-y], [-z], [-x]]	C_1
A31	[[y], [-x], [x], [-y], [-z], [-x]]	C_1
A32	[[y], [-x], [-x], [-z], [z], [-y]]	C_1
A33	[[y], [-x], [y], [-y], [z], [-x]]	C_1
A34	[[y], [-z], [y], [-y], [x], [-x]]	C_1
A35	[[y], [-x], [x], [-y], [z], [-x]]	C_1
A36	[[y], [-x], [-y], [-y], [x], [-x]]	C_1
A37	[[y], [-z], [-x], [-y], [x], [-y]]	C_1
A38	[[y], [z], [-x], [-y], [x], [-y]]	C_1

In this way, 38 meridional conformers, A1-A38, and 16 bisected conformers, B1-B16, were obtained.

3.2 Structural optimization of the conformers

Using the semi-empirical PM6 method, all of the 54 conformers, A1-A38 and B1-B16, were optimized. [It is noted that among PM5, PM6, and PM7, only PM6 gave a reasonable structure for the present nickel(II) complex. That is, Ni-O-C-N moiety is known to be planar (dihedral angle Ni-O-C-N $\sim 180^\circ$) for the related formamide complexes [14,15]; however, PM5 and PM7 gave deformed struc-

Table 3. Bisected diastereomers [5]

No	Example	Point Group
B1	[[y+z], [x-z], [x-y], [-y-z], [-x+z], [-x+y]]	D_{3d}
B2	[[y+z], [-x-z], [x-y], [y+z], [-x-z], [x-y]]	D_3
B3	[[y+z], [-x+z], [-x-y], [-y-z], [x-z], [x+y]]	S_6
B4	[[y+z], [x-z], [-x+y], [-y-z], [-x+z], [x-y]]	C_{2h}
B5	[[y+z], [-x+z], [x-y], [-y-z], [-x+z], [x-y]]	C_2
B6	[[y+z], [-x+z], [x-y], [y-z], [-x+z], [-x-y]]	C_2
B7	[[y+z], [x-z], [-x-y], [-y-z], [x+z], [-x+y]]	C_2
B8	[[y+z], [-x+z], [-x-y], [-y-z], [x+z], [x-y]]	C_2
B9	[[y+z], [-x+z], [x-y], [y-z], [-x-z], [x-y]]	C_2
B10	[[y+z], [x-z], [-x+y], [-y-z], [-x+z], [-x+y]]	C_s
B11	[[y+z], [-x-z], [x-y], [-y-z], [-x+z], [x-y]]	C_1
B12	[[y+z], [-x+z], [x-y], [y-z], [-x+z], [x-y]]	C_1
B13	[[y+z], [-x-z], [-x+y], [-y+z], [-x-z], [x+y]]	C_1
B14	[[y+z], [-x+z], [-x-y], [-y-z], [x+z], [-x+y]]	C_1
B15	[[y+z], [-x-z], [-x+y], [-y-z], [-x+z], [x-y]]	C_1
B16	[[y+z], [-x+z], [x-y], [-y+z], [-x-z], [x+y]]	C_1

Figure 2. Numbering system (A) and an example of a conformer (B).

tures (dihedral angle Ni-O-C-N $\sim 140^\circ$ or $\sim 220^\circ$.) Surprisingly, all the isomers converted to either of only two conformers, C1 and C2, as summarized in **Table 4**. Subsequently, conformers C1 and C2 were structurally optimized by the DFT method. (We chose LC-BOP and LC-BLYP, because they previously gave reasonable results [16].) The finally obtained structures are shown in **Figure 3**, and the energy differences are listed in **Table 5**. The most stable and the second most stable conformers, C1 and C2, have *pseudo-S₆* structure and *pseudo-D₃* structure, respectively.

The energy differences between the conformers were concluded

Figure 3. Optimized conformers for $[\text{Ni}(\text{NMF})_6]^{2+}$ complex cation (LC-BOP/6-31G). **Figure 4.** Two types of $[\text{Ni}(\text{NMF})_6]^{2+}$ cations (A and B) observed in a single crystal [15].

to be 1.8–2.2 kcal mol⁻¹ (**Table 5**), and if the ratios of the conformers are estimated using the Boltzmann's distribution law (kT product is 0.596 kcal mol⁻¹ at 300 K), the ratio of conformer C1 is more than 96%. Therefore, conformer C1 (*pseudo-S₆*) is practically the only species at room temperature.

3.3 Comparison with crystal structure

The crystal structure of $[\text{Ni}(\text{NMF})_6](\text{BPh}_4)_2$ was determined by single-crystal X-ray method [15]. In the crystal, there were two types of $[\text{Ni}(\text{NMF})_6]^{2+}$ cations, A and B (**Figure 4**), and both have *pseudo-S₆* structure. Therefore, the present computational investigation is consistent with the crystal structure.

4 CONCLUDING REMARKS

In this study, the structures of $[\text{Ni}(\text{NMF})_6]^{2+}$ complex cation were computationally obtained, and the result was consistent with the crystal structure. At the beginning, 54 possible conformers

Table 4. Optimized diastereomers for $[\text{Ni}(\text{NMF})_6]^{2+}$

No	Point Group	Initial structure
C1	<i>pseudo-S₆</i> (C_1)	[A3-A5, A7, A8, A10-A16, A21, A22, A24, A27-A37, B1, B3, B4, B8, B14, B15]
C2	<i>pseudo-D₃</i> (C_1)	[A1, A2, A6, A9, A17-A20, A23, A25, A26, A38, B2, B5-B7, B9-B13]

Table 5. Energy difference (kcal mol⁻¹) between two diastereomers (C1 and C2) of [Ni(NMF)₆]²⁺

DFT method	Energy difference [$E(C2) - E(C1)$]
LC-BOP/6-31G	2.876
LC-BOP/6-31G*	1.900
LC-BOP/6-31G**	1.849
LC-BLYP/6-31G	3.110
LC-BLYP/6-31G*	2.284
LC-BLYP/6-31G**	2.173

were obtained by the CGT method. Subsequently, the 54 conformers were structurally optimized by the semi-empirical PM6 method to obtain only two conformers, *pseudo-S₆* conformer and *pseudo-D₃* conformer. After the subsequent optimization by the DFT method, the energy difference indicated that the *pseudo-S₆* conformer is considered to be practically the only species at room temperature. This result is consistent with the fact that only the *pseudo-S₆* conformer was found in the crystal structure.

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