Effect of Molecular Distortion of Ligand Field Splitting in Five-Coordinated Metal Complex

Yoshiki Fujikawa,1 Dan Tsuneda,1 Yuki Tsutsumi,1 Momoe Nakano,1 Takeyoshi Oguma,1 Tomohiko Ishii,1 Genta Sakane,2 And Kazuyoshi Ogasawara3

1Program of Advanced Materials Science, Department of Engineering and Design, Faculty of Engineering and Design, Kagawa University, 2217-20 Hayashi-cho, Takamatsu, Kagawa 761-0396, JAPAN.
2Department of Chemistry, Faculty of Science, Okayama University of Science, 1-1 Ridaicho, Kita-Ku, Okayama 700-0005, Japan
3School of Science and Technology, Kwansei Gakuin University, 2-1 Gakuen Sanda, Hyogo 669-1337, JAPAN.

s19g572@stu.kagawa-u.ac.jp

Abstract. Metal complex indicates the significant physical properties such as magnetism, electrical conductivity and an optical property due to the electronic interaction between the ligand molecule and the central metal ion. We have evaluated the magnetism of the metal complex by controlling the ligand field splitting, which is the energy splitting of the d-orbitals. The magnetic phenomenon of such compounds are realized as a result of the electronic state based on the transition metal coordination complexes, and which can be switched between high spin (HS) and low spin (LS), that is called a spin-crossover (SCO) phenomenon. Our group have been investigated the way how to control the spin state according to the concept of a molecular distortion. The five-coordinated metal complex \(ML_5\) has been experimentally confirmed to be a molecular distortion called the Berry pseudorotation (BPR). In the BPR process, both the axial and equatorial ligands can move at the same rate of increasing the angle between the other axial or equatorial ligands in five-coordinated metal complex. The classical BPR mechanism changes its molecular symmetry between two independent trigonal bipyramidals (TBPs) of \(D_{3h}\) symmetry via a square pyramidal (SP) of \(C_{4v}\) symmetry. The distortion parameters in the five-coordinated metal complexes \(\tau_5\) are proposed in order to represent the distortion of the BPR process quantitatively. In this work, we predicted the possibility of the SCO phenomenon in intramolecular exchange mechanism through the BPR process in a five-coordinated metal complexes.

1. Introduction

In recent years, there are a wide variety of metal complexes, and in addition to the significant functional properties (such as magnetism, conductivity and optical property) often found in inorganic compounds, they have significant molecularness and design of organic compounds. Because of this, a number of studies are underway. As factors to determine the physical properties of metal complexes, it is necessary to consider ligand field splitting and electron configuration, which are the energy splits among five d-orbitals of the central metal ion. This ligand field splitting differs depending on the central metal and the ligand, and this changes the spin state, and it is possible to take two states of high spin or low spin. A phenomenon in which the spin states are interchanged by applying external field
stimulation (for example, heat, magnetic field, pressure or light) if the energy difference between the two spin states is slightly is called a spin-crossover (SCO) phenomenon. Therefore, our group have been investigated the way how to control the spin state according to the concept of a molecular distortion. In five-coordinate complexes, an intramolecular transfer phenomenon called Berry pseudorotation (BPR) has been reported experimentally (Scheme 1). The classical BPR mechanism changes its molecular symmetry between two independent trigonal bipyramids (TBPs) of $D_{3h}$ symmetry via a square pyramidal (SP) of $C_{4v}$ symmetry. The distortion parameters in the five-coordinated metal complex $\tau_5$ are proposed in order to represent the distortion of the BPR process quantitatively. In TBP, $\tau_5 = 1$ and SP becomes $\tau_5 = 0$.

$$\tau_5 = \frac{\theta_{ax} - \theta_{eq}}{60^\circ} \quad (0 \leq \tau_5 \leq 1)$$

$\theta_{ax}$ : Bonding angle of ax to ax
$\theta_{eq}$ : Bonding angle of eq to eq

W. Addison et al., Dalton Trans., 1349-1356 (1984).

![Scheme 1. Berry pseudorotation (BPR) process.](image)

However, In the five-coordinated complex where all the ligands are equivalent ML$_5$, the SCO couldn’t confirmed in BPR process. Therefore, in this work, in the monosubstituted five-coordinate complex ML$_4$L’ in which one of the ligands is substituted, the change of the spin state can be confirmed, and the spin state can be controlled from the bulkiness of the substituted ligand molecule.

2. Calculating Method

2.1. monosubstituted five-coordinate complex

Two patterns are possible only if the mono-substituted five-coordinate complex undergoes a structural change by Berry pseudorotation. This is distinguished by whether the central axis of the pseudorotation is a substituent. In the monosubstituted five-coordinates of this study, there are two patterns of pseudorotation, in which the central axis ligand is a cyano group (-CN) or a group of 15 pnictogen element substituents. In these two kinds of pseudorotations, the former is called a non-degenerate type Berry pseudorotation because the position of the ligand changes before and after the pseudo-rotation, while the latter is called a degenerate type Berry pseudorotation because the position of the ligand does not change before and after the pseudorotation (see Figure 1).

![Figure 1. The Berry pseudorotation of a monosubstituted five-coordinate complexes (Upper: degenerate process, Lower: non-degenerate process)](image)
2.2. Calculation model
The energy state and the steric barrier of the five-coordinate complex in Berry pseudorotation are different depending on the substituted ligand. In this work, a total of 15 cluster models were created, in which a pentacyano complex $[\text{Fe}^{2+}(\text{CN})_5]_\text{s}$ was used as the basic structure, and $X\text{H}_3$, $X\text{Me}_3$, and $X\text{Bu}_3$ were coordinated to five kinds of group 15 pnictogen atoms ($X$ denotes a pnictogen element, $X = N, P, As, Sb$ and $Bi$) respectively. In making the model, the carbonyl (-CO) complex, which was studied by Tsuneda et al. in our group, was used as a reference, and the atomic bond distances are shown in Table 1.

![Table 1. Atomic distances of monosubstituted five-coordinate complexes.](image)

3. Results and discussion
3.1 ML₅ five-coordinate complex with equivalent ligands
First, we show the results of the ligand field splitting and spin states of $[\text{Fe}^{2+}(\text{CN})_5]_\text{s}$ ML₅ with the equivalent ligand with no substituted. Then, the ligand field splitting $\Delta$ in the BPR process which becomes TBP again from TBP via SP is $\Delta = 2.329, 2.509$ and $2.330$ eV, respectively, and it is expected that SCO will not occur and keep the intermediate spin state (Figure 2).

![Figure 2. Multiplet energy diagram of $[\text{Fe}^{2+}(\text{CN})_5]_\text{s}$ ML₅.](image)

Figure 2 shows the multiplet energy diagram of $[\text{Fe}^{2+}(\text{CN})_5]_\text{s}$ ML₅ in the Belly pseudorotation process. In Figure 2, the horizontal axis is the distortion parameter $\tau_5$, and the vertical axis is the multiplet energy level. The spin states in the process of changing the distortion parameter from $-1$ to 1 were plotted by the DVME method. In this complex, by using a CN group having a very strong coordination ability as a ligand, the ligand field splitting became larger, and the spin state continued to keep the intermediate spin.
3.2. ML\textsubscript{L’} Monosubstituted five-coordinated complexes substituted with group 15 pnictogen.

The ligand field splitting and the spin state in the structural change of BPR in each substituent are shown in Tables 2 and 3 for the substituted five-coordinate complex ML\textsubscript{L’}, respectively.

**Table 2.** Spin state and ligand field splitting in each substituent, and SCO $\tau_5$ values (Degenerate type).

| Substituent | TBP ($\tau_5 = 1$) | SP ($\tau_5 = 0$) | TBP ($\tau_5 = 1$) |
|-------------|---------------------|--------------------|---------------------|
| NH$_3$      | Spin Intermediate 1.988 | Intermediate 2.239  | Intermediate 1.987  |
| PH$_3$      | Intermediate 2.113   | Intermediate 2.689  | Intermediate 2.107  |
| AsH$_3$     | Intermediate 1.987   | Intermediate 2.614  | Intermediate 1.984  |
| SbH$_3$     | Intermediate 2.159   | Intermediate 2.652  | Intermediate 2.163  |
| BiH$_3$     | Intermediate 2.112   | Intermediate 2.624  | Intermediate 2.115  |
| NMe$_3$     | Intermediate 1.927   | Low 2.254           | Intermediate 1.924  |
| PMe$_4$     | Intermediate 2.944   | Low 2.777           | Intermediate 2.382  |
| AsMe$_3$    | Intermediate 2.247   | Low 2.722           | Intermediate 2.246  |
| SbMe$_3$    | Intermediate 2.367   | Low 2.637           | Intermediate 2.372  |
| BiMe$_3$    | Intermediate 2.428   | Low 2.570           | Intermediate 2.392  |
| N$^1$Bu$_3$ | Intermediate 1.956   | Intermediate 2.197  | Intermediate 2.005  |
| P$^1$Bu$_3$ | Intermediate 2.087   | Low 2.603           | Intermediate 2.075  |
| As$^1$Bu$_3$| Intermediate 1.963   | Intermediate 2.535  | Intermediate 1.978  |
| Sb$^1$Bu$_3$| Intermediate 2.625   | Intermediate 2.560  | Intermediate 2.620  |
| Bi$^1$Bu$_3$| Intermediate 2.233   | Intermediate 2.545  | Intermediate 2.242  |

**Table 3.** Spin state and ligand field splitting in each substituent, and SCO $\tau_5$ values (Non-degenerate type).

| Substituent | TBP ($\tau_5 = 1$) | SP ($\tau_5 = 0$) | TBP ($\tau_5 = 1$) |
|-------------|---------------------|--------------------|---------------------|
| NH$_3$      | Spin 2.147 Intermediate 2.320 Intermediate 2.262 | 0.13 and 0.33 |
| PH$_3$      | Intermediate 2.018   | Intermediate 2.206  | Intermediate 2.217  |
| AsH$_3$     | Intermediate 1.921   | Intermediate 2.106  | Intermediate 2.095  |
| SbH$_3$     | Intermediate 2.047   | Intermediate 2.231  | Intermediate 2.214  |
| BiH$_3$     | Intermediate 1.987   | Intermediate 2.179  | Intermediate 2.157  |
| NMe$_3$     | Intermediate 1.565   | Intermediate 1.855  | Intermediate 1.907  |
| PMe$_4$     | Intermediate 2.057   | Intermediate 2.209  | Intermediate 2.202  |
| AsMe$_3$    | Intermediate 1.977   | Intermediate 2.152  | Intermediate 2.170  |
| SbMe$_3$    | Intermediate 1.811   | Intermediate 1.973  | Intermediate 1.976  |
| BiMe$_3$    | Intermediate 1.557   | Intermediate 1.766  | Intermediate 1.711  |
| N$^1$Bu$_3$ | Intermediate 1.333   | Intermediate 1.685  | Intermediate 2.311  |
| P$^1$Bu$_3$ | Intermediate 1.867   | Intermediate 2.090  | Intermediate 2.055  |
| As$^1$Bu$_3$| Intermediate 1.769   | Intermediate 2.015  | Intermediate 1.995  |
| Sb$^1$Bu$_3$| Intermediate 1.777   | Intermediate 1.979  | Intermediate 1.954  |
| Bi$^1$Bu$_3$| Intermediate 1.689   | Intermediate 1.889  | Intermediate 1.854  |

In the axially substituted degenerate Berry pseudorotation, spin state switching (Intermediate spin $\rightarrow$ Low spin) is predicted for complexes substituted with Me$_3$ group. In addition, non-egenerate Berry pseudorotation substituted at equatorial position could not predict the SCO. It could be predicted that in either pattern it is easy to take the low spin state in the SP structure. This can be explained as controlling the spin state using chemical pressure caused by the steric bulk of the substituted ligand. Next, Figure 3. shows the multiplet energy diagram of each complex using the DVME method.
Figure 3. Multiplet energy diagram of all degenerate Berry pseudorotations.

The degenerate type Berry pseudorotations in the axial position were arranged in the order of XH$_3$, XMe$_3$, and X$^1$Bu$_3$, and in the order of increasing atomic numbers of the group 15 pnictogen atoms (X = N, P, As, Sb and Bi) from the left.

Figure 4. Multiplet energy diagram of all non-degenerate Berry pseudorotations.

Substituents containing XMe$_3$ may be expected to the SCO phenomenon, but even if other complexes have SP structures, it seems that SCO may be possible with a little stimulation.

4. Conclusion
The SCO phenomenon was predicted for the spin state in the Belly pseudorotation using the molecular distortion of the five-coordinate complex ML$_5$ with equivalent ligands and the five-coordinate complex monosubstituted ML$_4$L$'$ with a group 15 pnictogen atom. From the results, it was predicted that SCO would not occur in a five-coordinate complex with an equivalent ligand ML$_5$, but it is
possible to be easy to switch low spin at the SP structure in both degenerate and non-degenerate pathways by monosubstitution ML₄L’. This explains the control of the spin state using chemical pressure causes by the steric bulk of the ligand. We can control the spin switching from intermediate spin to low spin from the bulkiness of the ligand by molecular distortion and found the possibility of SCO.

References
[1] W. Addison et al., Dalton Trans, pp. 1349 -1356, 1984.
[2] Dan Tsuneda, graduation thesis, 2015.