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研究課題名(和文) Switching of Orbital Angular Momentum Using the Dynamic Bond

研究課題名(英文) Switching of Orbital Angular Momentum Using the Dynamic Bond

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研究成果の概要(和文)：6と7の間の配位数の切り替えを示すCo(II)錯体が開発されました。この協調的な動的結合スイッチングは、リガンドフィールドのかなりの変調を引き起こし、それによって軌道角運動量の実質的な消光と回復をもたらします。このスイッチングメカニズムは、スピン多重度でスイッチングを示すスピncross-overおよび原子価互変異性化合物のメカニズムとはまったく異なります。

研究成果の学術的意義や社会的意義

This work has realized the largest reported change for any crystalline molecular material with reversible orbital angular momentum switching. This technique of switching coordination number by dynamic bond could be widely used to control various physical properties not only orbital angular momentum.

研究成果の概要(英文)：A Co(II) complex that exhibits coordination number switching between six and seven was developed. This cooperative dynamic bond switching induces considerable modulation of the ligand field, thereby leading to substantial quenching and restoration of the orbital angular momentum. This switching mechanism is entirely different from those of spin-crossover and valence tautomeric compounds, which exhibit switching in spin multiplicity.

研究分野：Coordination Chemistry

キーワード：magnetic switching orbital angular momentum dynamic bond

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## 様式 C - 19、F - 19 - 1、Z - 19 (共通)

### 1 . 研究開始当初の背景

Magnetic properties arise from the spin and the orbital angular momentum of electrons contained in a compound. Most of researches focus on controlling the spin state to realize the magnetic switching. In fact, the orbital angular momentum is the main physical contribution to magnetic anisotropy and plays an important role in various functional materials including molecular magnets and spintronic materials. Thus, to control the orbital angular momentum is a significant and amazing topic. However, there is no effective method currently to comprehensively modulate the orbital angular momentum via external stimuli. This is mainly because the orbital angular momentum of electrons is quenched by orbital hybridization and symmetry reduction; and only a fraction of them persist in some compounds restored by the spin-orbit coupling. The other fact is that the orbital angular momentum is not so sensitive to the distortion of coordination environment in the metal center, which have confirmed in our previous reported, as that of spin angular momentum.

### 2 . 研究の目的

The purpose of this research is to develop an efficient method for controlling the contribution of the orbital angular momentum and then to realize a great magnetic change. Additionally, we want to better understand the relationship between switching of orbital angular momentum and the dynamic structure to improve the method.

### 3 . 研究の方法

Considering the orbital angular momentum can be partially restored through spin-orbit coupling, which is associated with the energy gap between the excited states and the ground state, our strategy is based on the idea that the contribution of orbital magnetic momentum can be controlled by switchable ligands, that will change the coordination environment of the paramagnetic metal centers, thus leading to a corresponding electronic structure change. In this research, we have tried to switch the coordination number because our previous results have confirmed that varying the ligand field strength or switching the symmetry bring very small change in the magnetic susceptibility. In contrast to the ligand field strength, the coordination number is a discrete, rather than smoothly variable, property, and the resulting magnetic states should be more robust to changes in the environment.

To realize switching the coordination number, we introduced the dynamic bond that can undergo reversible breakage and reformulation with metal center under a given external stimuli. We used the nitrate and carboxylate ions as the donor of the dynamic bond though the coordination isomerization. The metal center we used is the Co(II) ion, which typically has large unquenched orbital angular momentum.

### 4 . 研究成果

A cobalt(II) complex,  $[\text{Co}(\text{NO}_3)_2(\text{L})]$  (complex **1**, L = ethyl-2,6-di(1H-pyrazol-1-yl)isonicotinate) exhibited a structure phase transition at 128.5 K. This complex exhibits the reversible coordination number change from seven at low temperature phase to six at high temperature phase through the coordination mode isomerization of the nitrate (Figure 1a). The structure analysis shows that the main structural change is the coordination number. The bond length of Co-O(N) bonds are consistent well with that of the high spin Co(II) complexes. The magnetic susceptibility exhibits the 10–11% change at the phase transition temperature (Figure 1b). This change may be the contribution of the orbital

angular momentum.

This change has explained well by theoretical calculations and variable temperature XAS spectra. The calculated magnetic susceptibility is consistent well with the experiment data. Without inclusion of spin-orbit coupling (SOC), the ground states of both phases are orbital singlets and well separated from their first two excited states ( $3841\text{ cm}^{-1}$  LT and  $1397\text{ cm}^{-1}$  for HT) due to the low symmetry, and orbital contribution should be completely quenched (Figure 1c). However, owing to SOC perturbation, the wavefunction of the excited states are mixed into that of the ground state with complex coefficients. Therefore, the orbital angular momentum has been partially recovered. The formation of the seventh bond modulates the ligand field causing an increase in the energy of the first singly occupied d-orbital and the breaking of the bond conversely lowers its energy, which induces effective quenching and restoration of the orbital angular momentum. This change is the largest reported value for any crystalline molecular material that exhibits thermally reversible orbital angular momentum switching.

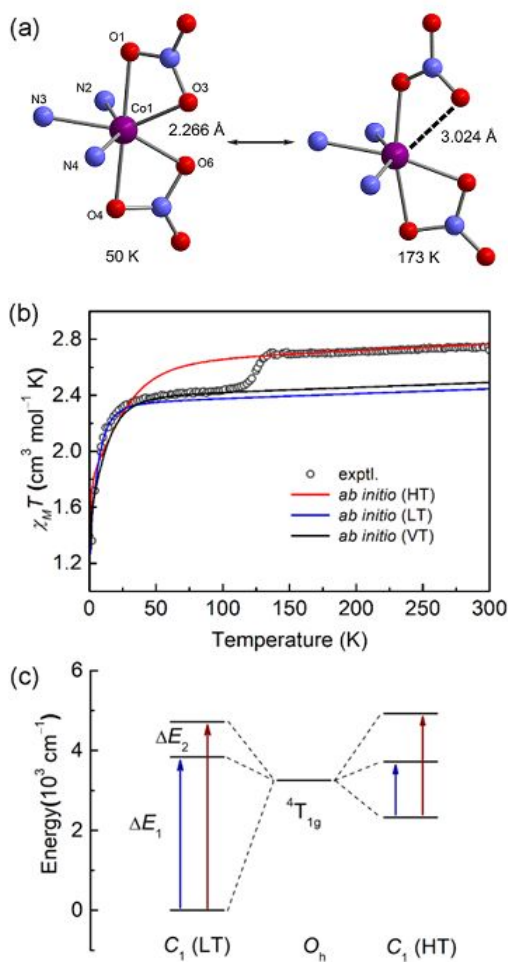


Fig. 1 (a) The coordination number was changed by the dynamic bond. (b)  $\chi_M T$  curves for complex 1 and the virtual molecule obtained from ab initio calculations. The calculated  $\chi_M T$  values in the low- and high-temperature phases are both slightly underestimated. The changes are well consistent with the experimental data. (c) Energy level diagram showing the splitting of the free ion quartet states under the influence of a ligand field with  $C_1$  symmetry in the low-temperature and high-temperature phases. The arrows depict the transitions calculated.

## 5. 主な発表論文等

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〔図書〕 計0件

〔産業財産権〕

〔その他〕

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6. 研究組織

	氏名 (ローマ字氏名) (研究者番号)	所属研究機関・部局・職 (機関番号)	備考
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