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Development of hydrazone complex salt exhibiting intermolecular proton transfer

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Abstract

My research focus on developing transition metal complexes exhibiting proton transfer. When the protons are removed from the metal complex, the ligand field change significantly. As a result, if proton transfer can be controlled by external stimuli such as electric field, some properties like spin state and color also can be controlled. In this study, I aim to erect how to design the complex salt exhibiting proton transfer based on a Ni complex. In terms of this purpose, acylhydrazone complex was synthesized as proton acceptor, while dicarboxylic acid play the role of proton donor. As a result, new compound with intermolecular short hydrogen bond was synthesized. It is expected to exhibit proton transfer by electric field.

1. Introduction

Hydrogen bond has played important role in almost all areas of chemistry, and it has been studied from the aspects of physical properties and material development like crystal engineering. Recently, in the field of ferroelectric material, the proton transfer type ferroelectric compounds which have polarization resulting from proton transfer through hydrogen bonds have been reported in succession [1]. These studies suggested to apply proton transfer phenomenon as a switching mechanism, because proton transfer influences molecular electronic state significantly and proton can be controlled by electric field. Based on these studies, the development of multifunctional materials coupled with proton transfer have been researched actively. For example, Mori et al reported new multifunctional an organic compound that magnetic and conductive properties tuned by intermolecular proton migration [2]. It is known that some transition metal complexes exhibit very interesting phenomena like spin transition or color change induced by subtle change in the ligand field. While enable them to be to storage material. If the proton transfer mechanism is successfully applied to such transition metal complexes, we are able to control some properties like spin state or color through the

proton transfer mechanism (Figure 1). However these attempts have not been successful so far due to the design principle of compound is not well defined. So in this study, I aim to elucidate the strategy to construct complex salts exhibiting possible proton transfer based on a Ni complex.

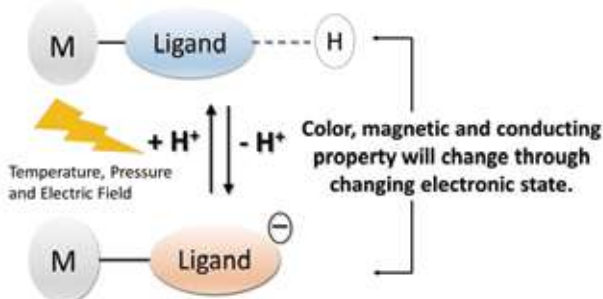


Fig. 1. Outline of proton transfer effect.

2. Design of compound

2.1. Design of ligand

As a precondition to realize proton transfer complexes, the ligands must have proton donor or acceptor sites because proton transfer occurs through hydrogen bonds. As an acceptor type ligand, I focused on acylhydrazone ligands (Figure 2). This type of ligands is tridentate ligand, and they can form proton acceptor site through deprotonation of N-H part. In this study, I treated with 2-pyridinecarboxyaldehyde-4-methylbenzoylhydrazone (= L) that R part is Me.

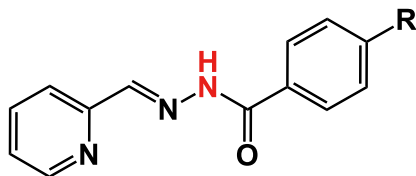


Fig. 2. Structural formula of acylhydrazone ligand.

2.2. Design of hydrogen bond

In order to make intermolecular hydrogen bonds, proton acceptor complex need to react with proton donor molecules. In this study, meso-2,3-Dibromosuccinic(Br₂Suc) acid is used as proton donor. In order to synthesize acylhydrazone complex salt with hydrogen bonds between proton donor and acceptor sites, acylhydrazone complex is need to accept protons from proton donor. However the pK_a value of hydrazone complex is lower than common carboxylic acid like acetic acid, so stronger acid decorated by halogen should be employed.

3. Experiment

3.1. Synthesis of Ni complex (1)

Ligand (L) (20 mmol) was dissolved in acetonitrile (30 ml) by heating under reflux. Thereafter, Et₃N (20 mmol) was added to this solution and the resultant reaction mixture was heated under reflux for 15min, followed by addition of nickel(II) perchlorate hexahydrate (10 mmol) to give a brown solution. This mixture was stirred briefly and then filtered, through slow evaporation of the solution at room temperature over several days, brown-red crystals of complex **1** were obtained.

3.2. Synthesis of Complex-dicarboxylic acid salt

Complex **1** (0.1 mmol) was dissolved in MeOH (15 ml). Thereafter, Br₂Suc (0.1 mmol) was added to this solution and resultant reaction mixture was filtered, on slow evaporation of the solvent at room temperature over several days, brown plate-like crystal of purpose compound **2** was deposited. Crystal structure of this compound were determined by single crystal single-crystal X-ray analysis.

4. Result and discussion

The chemical formulation of **2** is determined to be [Ni(L)₂](Br₂Suc) · 2MeOH by elemental analysis. Crystal structure of **2** is shown in Fig. 3. In this compound, two type hydrogen bond is formed between complex and dicarboxylic acid (2.569 Å) and dicarboxylic acid and dicarboxylic acid (2.465 Å). The distance of the hydrogen bonds are short, so it is hoped to exhibit proton transfer by electric field.

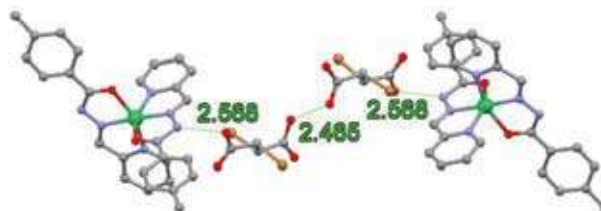


Fig. 3. Crystal structure and hydrogen bond distance of **2**

Electric field responsibility is measured now, and the result will be presented at poster session.

5. Conclusion

In this study, I aim to elucidate a strategy to design complex exhibiting proton transfer. In order to realize this, acylhydrazone type ligand was used to synthesize the complex as proton accepters. To form intermolecular hydrogen bond, meso-2,3-dibromosuccinic acid (Br₂Suc) was reacted with the complex. As a result, [Ni(L)₂](Br₂Suc) · 2MeOH can be synthesized which forms two types short hydrogen bonds. It is hoped to exhibit proton transfer induced by electric field.

Reference

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- [2] Akira, U.; Shota, Y.; Takayuki, I.; Hiromichi, K.; Akiko, N.; Reiji, K.; Hironori, N.; Youichi, M.; Kaoru, Y.; Yutaka, N.; Hatsumi, M. *J. Am. Chem. Soc.* **2014**, 136, 12184.

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