Solid-state high-resolution NMR studies on spin density distribution of a ferromagnetic coordination polymer: Ni(NCS)$_2$(Him)$_2$

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Abstract

We determined hyperfine coupling constants (hfcc) of the imidazole ligand in a ferromagnetic coordination polymer, di-μ-thio-cyanatobis(imidazole)nickel(II), using ^{1}H-, ^{2}H-, and ^{13}C-MAS-NMR. Partially or fully deuterated sample was prepared to measure temperature dependence of the isotropic shifts of NMR signals. We obtained hfcc of A_C = +0.57, +0.69, +1.88 MHz for 2-, 4-, 5-carbon and A_H = +0.66, +0.37, +0.48, +0.53 MHz for 1-, 2-, 4-, 5-proton in the imidazole ligand, respectively, which indicates that unpaired electron in $d_{x^2-y^2}$ orbital of Ni(II) ion delocalizes over the imidazole ligand. On the basis of the NMR and DFT results, we proposed an interchain superexchange pathway through N–H···S hydrogen bond.
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1. Introduction

Magnetic interactions in coordination compounds can be classified into three groups: direct, intramolecular, intermolecular interactions. The direct interaction is the interaction between paramagnetic metal ions connected by direct metal–metal bond. The other two interactions are mediated by diamagnetic ligands and are indispensable for a molecule-based magnet to exhibit long range order such as ferromagnetism, ferrimagnetism, and antiferromagnetism [1,2]. The intramolecular magnetic interaction is the interaction mediated by bridging ligands in a polynuclear complex. Not only simple ligands (Cl$^-$, Br$^-$, O^{2-}, OH$^-$) but also bidentate ligands (SCN$^-$ [3], ox$^-$ [4], N$_3$$^-$ [5]) can act as a magnetic coupler. The role of these bridging ligands in the superexchange interaction can be explained well by a molecular orbital theory at the level of extended Hückel calculation. And the theory can be verified from spin

density distribution determined by polarized neutron diffraction experiment [6].

In contrast, the intermolecular magnetic interaction, which contains van der Waals contact or hydrogen bonding in its interaction pathway, has not been understood well because this interaction is relatively weak and it may depend on crystal packing. This interaction plays an important role when pseudo-low-dimensional magnetic compound undergoes three-dimensional ordered state. An example is diimidazolecopper(II) dichloride [7,8]. In this crystal, one-dimensional Cu(II) chain is formed by bridging Cl ion, and the magnetic susceptibility data above 12 K is interpreted by one-dimensional antiferromagnetic Heisenberg model with $J = -2.1$ cm^{-1}. However, it undergoes three-dimensional antiferromagnetic ordering below 7.7 K, indicating interchain antiferromagnetic interaction. This interchain interaction is probably mediated by N–H···Cl hydrogen bond between adjacent chains but its coupling mechanism is still unknown. Moreover, imidazole ligand seems to act as ferromagnetic coupler in another compound [3]. Higher level of theory and experimental methods to

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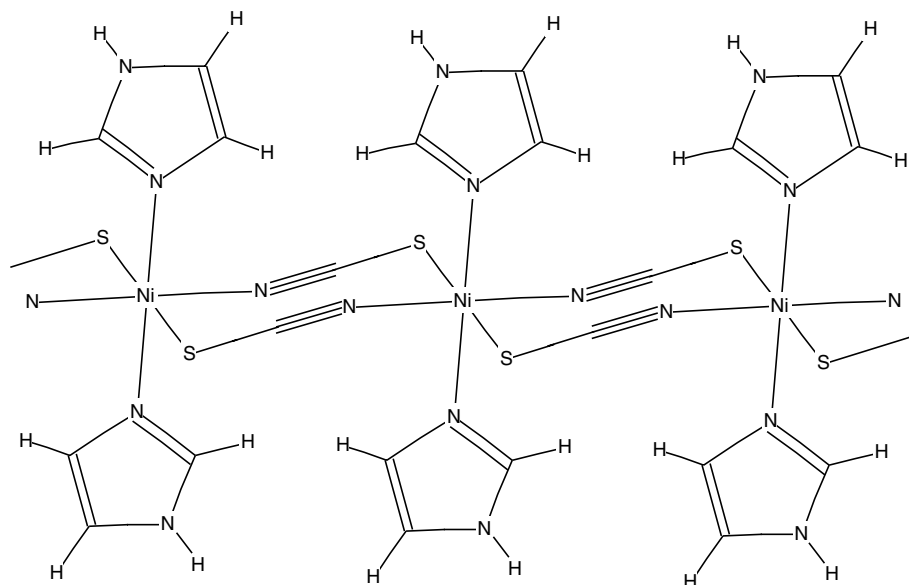*E-mail address:* maruta@sci.hokudai.ac.jp (G. Maruta).

Fig. 1. One-dimensional chain structure of Ni(NCS)$_2$(Him)$_2$.

verify this theory are necessary to understand the inter-molecular magnetic interaction in coordination compounds. In this work, we have employed Density functional theory (DFT) and NMR experiment [9] to elucidate role of the imidazole ligand in long range ordering.

Di-μ-thiocyanatobis(imidazole)nickel(II), Ni(NCS)$_2$(Him)$_2$, is a ferromagnet (T_C = 5 K) which consists of NCS-bridged one-dimensional Ni(II) chains as shown in Fig. 1 with the intrachain exchange interaction parameter (2J) of 8.0 cm^{-1} [3]. In this work, we determined electron spin density distribution of imidazole ligand in the compound by measuring solid-state high-resolution ^{1}H, ^{2}H, and ^{13}C NMR spectra in order to elucidate the interchain magnetic interaction essential for long-range order in the crystal. Partially or fully deuterated imidazole was used to prepare the sample and magic angle spinning (MAS) technique was employed to measure temperature dependence of the isotropic shifts of NMR signals. These experimental results indicate that unpaired electrons in the d-orbitals of the octahedral nickel(II) ion delocalize over the imidazole ligand. Consequently, we proposed an interchain superexchange pathway through N–H···S hydrogen bond.

2. Experimental

2.1. Preparations

1,2-Dideutero-imidazole was prepared by the literature method [10]. The degree of deuteration was estimated to be 70–80%. Ni(NO$_3$)$_2$ · 6D$_2$O was recrystallized from deuterium oxide. 1,2,4,5-Tetradeutero-imidazole (98% D, Cambridge Isotope Laboratories) and the other reagents were used as supplied. Non-deuterated sample of Ni(NCS)$_2$(Him)$_2$ (**1**) was prepared by a similar method described in [3]. Ni(NO$_3$)$_2$ · 6H$_2$O (2 mmol) and NaSCN (4 mmol) were dissolved in water (2 cm^3), then the aqueous solution was added to methanol solution (1 cm^3) of imidazole (4 mmol). The resulting blue solution was left to stand under N$_2$ gas flow at room temperature. Green crystal of Ni(NCS)$_2$(Him)$_2$ was obtained with violet crystal of Ni(NCS)$_2$(Him)$_4$. The products were separated by hand, washed with water and acetone, and dried in vacuo. Fully deuterated sample of Ni(NCS)$_2$(1,2,4,5-tetradeutero-Him)$_2$ (**4**) was prepared from 1,2,4,5-tetradeutero-imidazole with deuterated solvents of D$_2$O and CH$_3$OD. Partially deuterated samples of Ni(NCS)$_2$(1,2-dideutero-Him)$_2$ (**3**) and Ni(NCS)$_2$(2-deutero-Him)$_2$ (**2**) were prepared from 1,2-dideutero-imidazole with deuterated and protonated solvents, respectively.

2.2. NMR measurements

Solid-state high-resolution ^{1}H, ^{2}H, and ^{13}C NMR spectra of **1**–**4** were measured at a resonance frequencies of 300, 46.1, and 75.4 MHz, respectively, with a Bruker DSX300 spectrometer and a 4-mm CP/MAS probe. Temperature dependence of the spectra were measured for **3** from 300 to 200 K. MAS technique was used to obtain high-resolution spectra for the powder samples, whereas cross polarization or ^{1}H decoupling was not employed. The spinning rates of the samples were 9–10 kHz. The free induction decay (FID) of ^{1}H-MAS-NMR was accumulated from the first rotational echo after a π/2 pulse. For ^{2}H- or ^{13}C-MAS-NMR, π pulse