

IV-O Magnetic Local Structure and Magnetic Interactions in Molecule Based and Organic-Inorganic Hybrid Magnets

Organic ferromagnet is one of the realizations of great possibilities of organic molecules which can be designed to exhibit a variety of functions by chemical modifications and attracts interest of chemists in broad areas such as organic, physical, and theoretical chemistry, *etc.* Ferromagnetism of organic materials is of current interest. It is desired to clarify the mechanism of intermolecular magnetic interaction in a microscopic viewpoint to establish a leading principle to produce the ferromagnetic ordering in the crystalline phase of molecule based materials and to understanding the characters and the functions of open-cell molecules. Solid state high resolution NMR techniques provide an unique information of the magnetic local structure and the magnetic interactions in a microscopic view point. We have investigated the magnetic local structure and magnetic interaction for a variety of magnetic materials including a class of organic-inorganic hybrid magnetic materials. Botallackite-type compounds $\text{Cu}_2(\text{OH})_3\text{X}$ (X = exchangeable anion) exhibit layered structures, in which a nonequilateral planar triangular lattice of copper ions is constructed. The copper ions are bridged by hydroxide ions and exchangeable anions X to form infinite layers. A variety of anions X can be incorporated by anion-exchange in suspended solution and the bulk magnetism of $\text{Cu}_2(\text{OH})_3\text{X}$ is controlled by the property of X .

IV-O-1 Solid State High Resolution Deuterium NMR Study of Electron Spin Density Distribution of Hydrogen-bonded Organic Ferromagnetic Compound 4-Hydroxyimino-TEMPO

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Electron spin density distribution at hydrogen atoms of 4-hydroxyimino-2,2,6,6-tetramethylpiperidin-1-ylloxyl (4-hydroxyimino-TEMPO), which has been recently found to be a molecular ferromagnet at low temperature, was determined in the crystalline phase from the temperature dependence of the Fermi contact shifts of magic angle spinning deuterium NMR spectrum to elucidate the mechanism of intermolecular magnetic interaction. There are two kinds of close contacts among neighboring radical molecules in the crystalline phase. An axial methyl hydrogen atom locates closely to a neighboring N-O radical group and the hydroxyl group forms hydrogen-bonding with another neighboring N-O radical group. The plus and minus signs of observed hyperfine coupling constants A_D of methyl deuteriums indicate that two different mechanisms of electron spin density distribution exist. Equatorial CD_3 groups show negative coupling constants ($A_D = -0.24$ MHz) induced by the intramolecular spin polarization mechanism, whereas positive hyperfine coupling constants ($A_D = +0.12$ MHz) of axial CD_3 groups indicate that a single occupied MO spreads out partly toward the axial CD_3 groups by the mechanism of hyperconjugation. The small positive hyperfine coupling constant of the axial methyl group is brought about from averaging among one positive and two negative values of the three deuterium atoms of the methyl group due to rapid rotation. The intermolecular magnetic interaction through the axial methyl group seems to be sensitive to the orientation of the methyl group and it can be ferromagnetic in the crystal of 4-hydroxyimino-TEMPO. A large negative hyperfine

coupling constant ($A_D = -0.45$ MHz) observed for the NOD group strongly implies that the hydrogen-bonding mediates the intermolecular magnetic interaction in the crystalline phase. The experimental results and the molecular orbital calculations indicate that the ferromagnetic interaction exists in the hydrogen-bonded chains running along the crystallographic c axis and that the two chains are considered to be coupled ferromagnetically through the axial methyl groups to form a double chain. In the directions of crystallographic a and b axes, weak ferromagnetic interactions are expected from the measured spin density distributions of the deuterium atoms of the equatorial methyl and of the methylene groups which participate in inter-chain contacts in a crystallographic a - b plane.

IV-O-2 Magic Angle Spinning ¹H-NMR Study of the Spin Density Distribution of Pyridyl Nitronyl Nitroxides in the Crystalline Phase

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Electron spin density distribution was investigated for p - and m -pyridyl nitronyl nitroxides (p -PYNN and m -PYNN) in the crystalline phase by the temperature dependence of the solid state high-resolution ¹H-MAS NMR spectrum. The results were compared with that of phenyl nitronyl nitroxide (PNN) for elucidating the effect of incorporation of a nitrogen atom into the aromatic group. For p -PYNN, the magnitude of the negative spin density at 3 and 5 positions of the pyridyl group was suppressed by 30% in comparison with that of PNN and the positive spin density at 2 and 6 positions was slightly enhanced by 10%. On the other hand, the positive spin density at 2, 4 and 6 positions of pyridyl group of m -PYNN was suppressed by 30% in average and the negative one at 5 was also suppressed by 20%. The DFT calculation at UBLYP/6-31G(d,p) level suggested that the molecular geometry largely contributed to the change of the spin density in addition

to the effect of incorporation of the nitrogen atom. In fact, the spin density distribution of the aromatic ring of *p*-PYNN was remarkably reduced in solution compared with that in the crystalline phase.

IV-O-3 Local Magnetic Structure of Layered Compounds $\text{Cu}_2(\text{OD})_3\text{X}$ with Exchangeable Acid Anion X Studied by Solid State High Resolution Deuterium NMR

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The microscopic magnetic local structure of Botallackite-type layer structured compounds $\text{Cu}_2(\text{OD})_3\text{X}$ (X = NO_3^- and HCOO^-) exhibiting non-equilateral planar-triangular magnetic lattice was determined by the solid-state high-resolution deuterium NMR of deuterated hydroxy groups in the high temperature region above 190 K. The magnetic interactions in a copper ion layer were probed by the paramagnetic NMR shifts of the two chemically distinct hydroxy groups. Isotropic NMR shift of each hydroxy group showed different temperature dependence, suggesting non-uniform magnetic interaction. It appeared that the magnetic interaction in the copper layer could be decomposed to a sum of 1D-Heisenberg ferro- and antiferromagnetic chains in the high temperature region. Two distinct copper chains with ferro- and antiferromagnetic exchange interactions $J = +19 \pm 11$ and -21 ± 3 K were found for X = NO_3^- from the temperature dependence of the two distinct NMR signals, while $J = +13 \pm 7$ and -13 ± 5 K for X = HCOO^- . The derived values of J almost reproduced the temperature behavior of the magnetic susceptibility χ_{AT} vs. T .

IV-O-4 Solid State High Resolution NMR Studies of Electron Spin Densities in Charge-Transfer Complex-Based Organic Ferromagnets

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A variety of purely organic ferromagnets, which consist of stable neutral radical species, have been developed. Charge-transfer complex-based organic ferromagnets are particularly of current interest because

of their potential to exhibit ferromagnetism at high temperatures. In these compounds, donor (D^{\bullet}) and acceptor (A^{\bullet}) can be designed to bear electron spins and electronic conduction can be also expected, so that the magnetic interaction in these salts may be different from those in neutral radical-based magnetic crystals and a novel magnetism is expected. A series of 4,4,5,5-tetramethylimidazolin-1-oxyls with 4-(*N*-R-pyridinium) groups at the 2-position (1^{\bullet} : R = methyl, 2^{\bullet} : R = ethyl, 3^{\bullet} : R = *n*-propyl) form stable charge transfer complexes with the radical anion of TCNQF₄. It has been revealed by the magnetic susceptibility measurements that $1^{\bullet}\cdot\text{TCNQF}_4^{\bullet-}$ and $3^{\bullet}\cdot\text{TCNQF}_4^{\bullet-}$ are ferromagnets at low temperature ($T_c \sim 0.5$ K), whereas $2^{\bullet}\cdot\text{TCNQF}_4^{\bullet-}$ exhibits antiferromagnetic behavior. It is interesting to study the mechanism of magnetic interaction of these CT complexes. The mechanism can be elucidated from the electron spin density distribution in the magnetic crystals. In this work, we have determined the electron spin density distribution and the magnetic local structure in the salts of $1^{\bullet}\cdot\text{TCNQF}_4^{\bullet-}$, $2^{\bullet}\cdot\text{TCNQF}_4^{\bullet-}$ and $3^{\bullet}\cdot\text{TCNQF}_4^{\bullet-}$ by solid state high resolution ¹H, ¹³C and ¹⁹F-NMR.

IV-O-5 Variable Magnetism of Layer-Structured Compounds $\text{Cu}_2(\text{OD})_3\text{X}$ with Exchangeable Anion X: Magnetic Local Structure and Magnetic Interactions Determined by Solid-State High-Resolution Deuterium NMR

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The microscopic magnetic local structure of Botallackite-type layer-structured compounds $\text{Cu}_2(\text{OD})_3\text{X}$ (X = $\text{C}_6\text{H}_5\text{COO}^-$) was determined by the solid-state high-resolution deuterium NMR above 190 K. The magnetic interaction in a copper layer was probed by the isotropic NMR shifts of OD⁻ groups and could be approximated by a sum of 1D-Heisenberg chains in the high temperature region. Two copper chains with different exchange interactions $J = -54 \pm 4$ and -92 ± 3 K were found for $\text{Cu}_2(\text{OD})_3\text{C}_6\text{H}_5\text{COO}$ from the temperature dependence of the three distinct NMR signals. The derived values of J almost reproduced the high temperature behavior of the magnetic susceptibility χ_{AT} vs. T . The magnetic susceptibility of isotopic analogue $\text{Cu}_2(\text{OH})_3\text{C}_6\text{D}_5\text{COO}$ showed ferromagnetic interaction below 50 K. Electron spin distribution in a phenyl ring of a benzoate anion is governed by spin polarization mechanism and its magnitude is very small. Magnetic interaction between the layers through the benzoate anion is very weak.

IV-P Proton Transfer Tunneling in Interacting Hydrogen Bonds in the Solid State

Control of functional interactions, such as electronic and dynamic one, is a key to produce new functional materials. It is important to study the possibility of the functional interactions in the solid state. The nuclear magnetic resonance provides microscopic aspects of the functional interactions in the solid state. Hydrogen bond has a great capability for mediating a variety of interactions. We have investigated proton transfer dynamics in the interacting hydrogen bonds in organic quasi-conjugated π -system. Interaction between the hydrogen bonds is a key point for propagating an information of one hydrogen bond to the other hydrogen bond through molecular frame.

IV-P-1 Proton Dynamics in Interacting Hydrogen Bonds in the Solid State: Proton Tunneling in the NHO Hydrogen Bonds of N,N'-Di(2-Hydroxy-1-Naphthylmethylene)-*p*-Phenylenediamine

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Combination of comprehensive investigations of the spin-lattice relaxation rate of proton and low temperature ¹⁵N-CP/MAS NMR spectrum provides unique information of proton dynamics in two interacting NHO hydrogen bonds of solid N,N'-di(2-hydroxy-1-naphthylmethylene)-*p*-phenylenediamine (DNP). It was evidenced from the ¹H-NMR relaxation measurement that tunneling mechanism operates for the proton transfer in the hydrogen bonds. The tunneling phenomenon is closely related to the very small energy differences among the four tautomeric states accompanied with the proton transfer in the two NHO hydrogen bonds. The very small values of the energy difference, in spite of the chemically asymmetric NHO hydrogen bond, were revealed by the ¹⁵N-CP/MAS NMR spectrum. This is a unique character of solid DNP. It was also suggested from the derived energy scheme of the four tautomers and activation energies of the proton transfer that an interaction exists between the two NHO hydrogen bonds linked by π -electronic molecular frame. This means that the information of one NHO hydrogen bond, *e.g.* OH-form or NH-form, propagates to the other hydrogen bond and the proton transfer in one hydrogen bond induces the change of the potential function for the proton transfer in the other hydrogen bond.