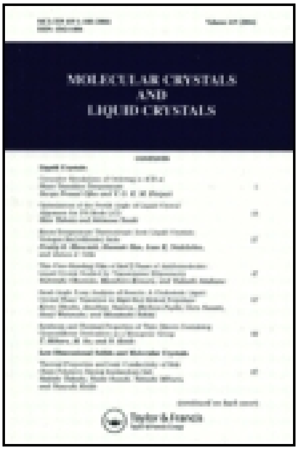

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Structure and Magnetic Property of 2-Imidazolylnitronyl Nitroxide and Its Metal Complexes

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STRUCTURE AND MAGNETIC PROPERTY OF 2-IMIDAZOLYLNITRONYL NITROXIDE AND ITS METAL COMPLEXES

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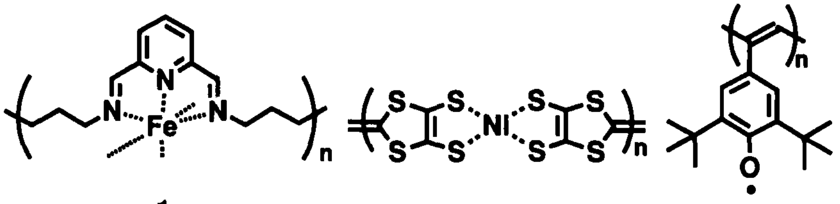
Abstract Structure and magnetic property of 2-(imidazole-2-yl)-4,4,5,5-tetramethyl imidazoline-1-oxyl-3-oxide and its metal complexes are studied in order to identify structure-property relationship.

INTRODUCTION

Recently, there has been substantial interest in the study of molecular-based magnetism. The syntheses of organic radicals, polyradical macromolecules, and coordination polymers have been in progress based on individual strategies.[1] Utilizing intermolecular magnetic coupling in crystals, purely organic radicals with bulk ferromagnetism at cryogenic temperature have been reported. Parallel to these efforts, one approach to design and synthesize polymeric high-spin organic molecules using long-range intramolecular magnetic coupling has been developed. The methodology involves the application of theoretical models of magnetic coupling to conjugated polymers bearing paramagnetic spin centers.[2] Another approach using organic radicals as a spin source is to build up coordination polymers in which the ferro- or ferri-magnetic chain is composed of metal ions and bridging radical ligands.[3]

According to these strategies, poly Schiff base iron complex **1**,[4] TTF-based nickel polymers **2**,[5] and radical-substituted polyacetylenes **3** [6] have been reported (Scheme 1). **1** showed ferromagnetic characteristics at room temperature due to coexisting iron oxide. **2** was chemically oxidized into mixed-valence state and exhibited high electrical conductivity, but expected magnetic interaction between metal ions through organic conjugated system could not be detected. In contrast to insoluble and infusible nature of **1** and **2**, highly soluble **3** and its analogues could be characterized by



1 2 3

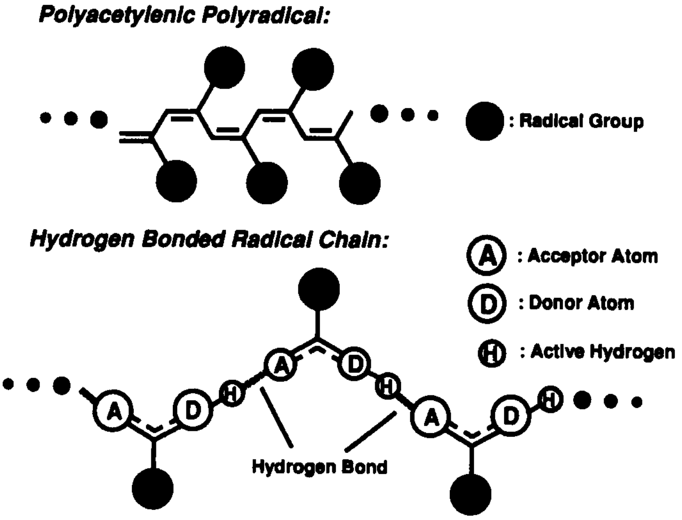
SCHEME 1

various spectroscopies. However, expected through-bond ferromagnetic coupling based on theoretical model was not observed in **3**. A non zero spin density distribution over the conjugated backbone structure is indispensable for strong through-bond interaction. The spin density at the polyene chain for **3** is not large enough to cause ferromagnetic coupling or to overcome through-space antiferromagnetic interactions between side-chain radical substituents. Amorphousness of **3** prevented the control of interchain spin coupling which is essential for bulk magnetism.

Among various intermolecular interactions, hydrogen bonds are strong in energy and whose directional properties are better understood than many other types of non-bonded interactions. Introduction of hydrogen-bonding sites into organic radicals is useful way of controlling molecular arrangement in crystal. So far various type of organic radicals with OH site have been reported and structurally characterized.[7] We have been interested in the electronic structure of imidazole derivatives which have both proton donor site (NH) and proton acceptor site (N), and their role of magnetic coupler in anion state.[8] Hydrogen bonding interactions have also been investigated from the point of coordination chemistry. Interesting coordination structures accompanying magnetic interaction have been reported in biimidazole complexes.[9]

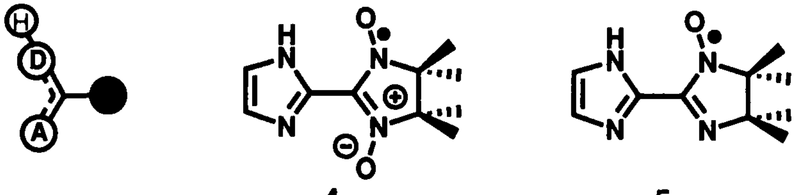
STABLE NITROXIDES WITH HYDROGEN BONDING SITE

The conjugated system in polyradical macromolecules may be replaced by hydrogen bonded chain if spin polarization through the hydrogen-bonding site occurs (Scheme 2). As a model system of hydrogen-bonded radical chain, we have designed and synthesized imidazole derivatives with stable radical at 2-position such as 2-imidazole-nitronylnitroxide **4** and -iminonitroxide **5**. **4** was prepared by coupling of 2-imidazolecarboxaldehyde and 2,3-dimethyl-2,3-bis(*N*-hydroxyamino)butane followed by chemical oxidation according to the method described in the literature.[10] **5** could be



SCHEME 2

isolated as a byproduct of 4 during column chromatography. 4 crystallizes in the centrosymmetric space group $P\,2_1/a$. In the crystal N-H...N hydrogen bonding chain with N...N distance of 2.811(6)Å is found as shown in Figure 1. Between the hydrogen bonded chains 4 formed spin pair within nitroxide oxygen atoms (3.483(5) Å). Magnetic susceptibility of 4 showed maximum at 110 K and minimum at 20 K. The magnetic data were fit to a Bleaney-Bowers expression of the magnetic susceptibility for a dimer. Non-linear curve fitting afforded singlet-triplet gaps, $2J = -122.8(1)\ \mathrm{cm}^{-1}$, with an agreement factor of 1.4×10^{-4}. The magnetic data can be interpreted by direct overlap between the magnetic orbitals of the two nitronylnitroxide at the paired site. Magnetic interaction through hydrogen bonded chain could not be observed in 4 because spin density distribution localized over nitronylnitroxide moiety. An antiferromagnetic interaction was



4 5

SCHEME 3

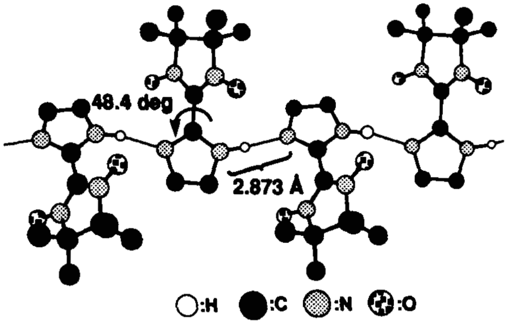


FIGURE 1 Hydrogen bonded chain observed in **4**.

also observed in **5**. Synthesis of new radicals with extended spin delocalization over imidazole ring is in progress.

MAGNETIC PROPERTY OF METAL COMPLEXES

4 and **5** could form complexes with various metal ion source. As an typical example molecular structure of **4**-Cu(ClO$_4$)$_2$ is shown in the Figure 2. The complex was a centrosymmetric tetragonally distorted octahedral species whose apical sites are occupied by the weakly coordinated perchlorate ion. The structural characteristics of the complex is relatively planar chelate ring compared to 2-pyridyl analogues. Intramolecular hydrogen bond was observed between imidazole NH site and non-coordinating site of nitoroxide oxygen, and intermolecular one also existed between NH and perchlorate oxygen of neighboring complex. Short copper-nitroxide oxygen distance (1.963(2) Å)

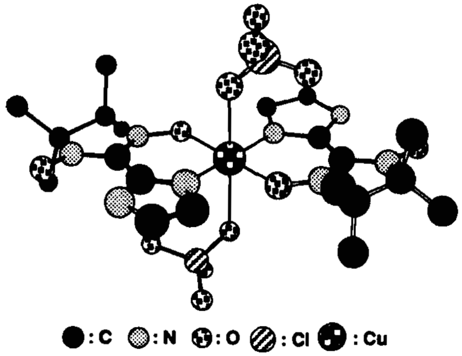


FIGURE 2 Molecular diagram of **4** - Cu(ClO$_4$)$_2$.

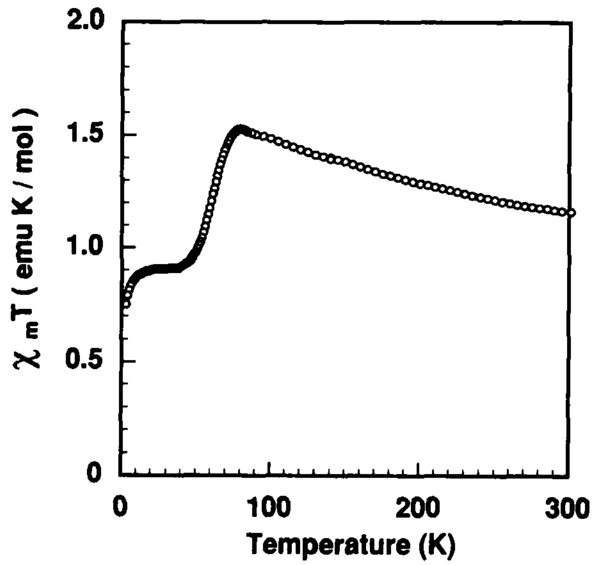


FIGURE 3 χ_mT vs T plot of 4 - $Cu(ClO_4)_2$ (cooling process).

and small difference in the NO bond length between coordinated site and non coordinated one suggested equatorial coordination by lone pair electrons.

Magnetic data of the complex is shown in the form of the temperature dependence of χmT value (Figure 3). χmT value at room temperature is 1.16 emu K/ mol, which is almost equivalent to the non interacting three spin system (= 1.125 emu K/ mol). The value rapidly increases with lowering of the temperature down to 75K and show maximum value of 1.51 emu K/ mol, and sudden decreases in χmT value below the temperature was observed. Interestingly the change in χmT value showed hysteresis loop between cooling process and heating one. Based on the crystal data of high temperature phase, increase in χmT value with lowering temperature can be explained by intramolecular ferromagnetic interaction due to orthogonality between magnetic orbitals. The existence of hysteresis in the magnetic susceptibility measurement suggests that the spin transition is cooperative phenomena in the hydrogen-bonded crystal. From the preliminary experiment, 4-$Ni(ClO_4)_2 \cdot xH_2O$ had intramolecular ferromagnetic interaction, but did not show any thermal hysteresis effect. Investigation on the detailed mechanism of spin transition in connection with hydrogen bond is under way.

Overall, the introduction of NH hydrogen bond site into stable organic radicals offers new methodology for assembling open shell molecules. The magnetic properties of these assembled radicals and radical complexes are expected to lead to applications as a magnetically condensed material.

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