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Crystal Structures and Magnetic Properties of Hydrogen-Bonded Nitronyl Nitroxide Radicals and Their Metal Complexes

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Nitronyl nitroxide derivatives showing hydrogen-bonded structures in the solid state have been prepared and characterized. In the complex of *p*-hydroxyphenyl nitronyl nitroxide with 1,2-Bis(diphenylphosphinoyl)ethane (**1**), water molecules are bridging the two organic components, forming a hetero-chain structure. 3,5-Dimethyl-4-hydroxyphenyl nitronyl nitroxide (**2**) and pyridone-substituted nitronyl nitroxide (**3**) were also prepared and shown to have 1-D hydrogen-bonded chains. The magnetic properties of these complexes are also discussed.

Keywords: nitronyl nitroxide; hydrogen bond; crystal structure

INTRODUCTION

Magnetism in organic molecular compounds has attracted considerable interest in recent years[1], and nitronyl nitroxides have proven to be useful building blocks for molecular-based magnets[2]. Introducing the hydrogen-bond is a useful method to organize molecular assemblies, and several organic radicals carrying hydrogen-bonding sites have been

reported. Typical examples are the phenol-substituted nitronyl nitroxides[3,4], which exhibit a variety of hydrogen-bonded network structures, and propagation of ferromagnetic interactions through the hydrogen bond is demonstrated in hydroquinone-substituted radicals[4]. Veciana *et al* also report an interesting compound of uracil-substituted radical[5]. More recently, transition metal complexes of organic radicals have attracted attention, such as metal salts of nitronyl nitroxide phenolates[6], which exhibit exchange coupling between the ligand radical and the metal center.

In this paper, we report the structures and magnetic properties of some hydrogen-bonded assemblies of nitronyl nitroxide derivatives: the complex of *p*-hydroxyphenyl nitronyl nitroxide with 1,2-Bis (diphenylphosphinoyl)ethane (**1**), 3,5-Dimethyl-4-hydroxyphenyl nitronyl nitroxide (**2**), and a pyridone-substituted nitronyl nitroxide (**3**). We further tried to obtain transition metal complexes of these radicals.

EXPERIMENTAL

p-Hydroxyphenyl nitronyl nitroxide was prepared according to the literature method[7]. Complex **1** was isolated unexpectedly by the reaction of the *p*-hydroxyphenyl radical and $NiCl_2$(dppe). Nitronyl nitroxide derivatives **2** and **3** were prepared from their aldehyde precursors according to the standard procedure[8].

X-ray diffraction data were collected on a Rigaku AFC-5S four-circle diffractometer using Mo$K\alpha$ radiation. Crystallographic data for **1**: Formula $C_{39}H_{43}N_2O_6P_2$, monoclinic, $P2_1/n$, a = 9.223(5) Å, b = 20.600(7) Å, c = 19.111(5) Å, β = 90.77(4) , V = 3630(2) Å^3, Z = 4, R_1 = 0.088 for 2539 observed reflections. Crystallographic data for **2**: Formula $C_{15}H_{21}N_2O_3$, monoclinic, $C2/c$, a = 16.787(4) Å, b = 13.299(6) Å, c = 14.290(3) Å, β = 110.62(2)°, V = 2985(1) Å^3, Z = 8, R_1 = 0.063 for 2432 observed reflections. Crystallographic data for **3**: Formula $C_{12}H_{16}N_3O_3$, monoclinic, $P2_1/a$, a = 7.603(1) Å, b = 19.093(4) Å, c = 8.919(1) Å, β = 104.92(1)°, V = 1251.2(4) Å^3, Z = 4, R_1 = 0.057 for 1285 observed reflections. Magnetic susceptibility data on microcrystalline samples were collected from 300 to 2.0 K using a SQUID susceptometer in a magnetic field of 2000 G.

RESULTS AND DISCUSSION

Hydrogen-Bonded Three-Component Complex with 1-D Structure

One-dimensional hydrogen-bonded structure of complex **1** is shown in Figure 1(a). This crystal contains water molecules, which are bridging the phenolic hydrogen of the radical and the neighboring phosphine oxides through hydrogen bonds, as shown in Figure 1(b). The hydrogen bonds thus constitute an interesting three-component chain. Perpendicular to this chain, the radical molecules show one-dimensional stacking arrangements. Although no short NO···ON distances could be found between the radical molecules, there exists an intermolecular close contact between the phenolic oxygen and the methyl group of the neighboring molecule, with the interatomic C–H···O distance of 3.21 Å.

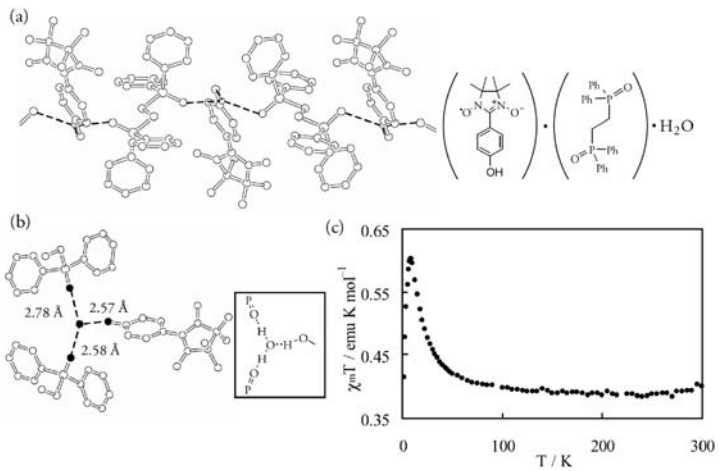

FIGURE 1. (a) 1-D chain structure of **1**. (b) Local structure of hydrogen bonding in **1**. (c) Plot of $\chi_m T$ vs T for **1**.

The magnetic susceptibility of **1** is shown in Figure 1(c). The $\chi_m T$ value showed a maximum at 8 K, and then decreased. The magnetic data could be analyzed in terms of a one-dimensional Heisenberg model[9]. The best fit parameter gave an intrachain ferromagnetic interaction of J/k_B = + 6.7 K. The origin of the ferromagnetic interaction can not clearly be interpreted at this stage, though one of the

possible mechanisms could be an interaction through the methyl hydrogen, as proposed by Nogami *et al.* to account for the ferromagnetic pathway in nitroxide radicals[10].

There are a few examples of multi-component magnetic materials composed of neutral radicals, and an interesting example among them is a two-component complex reported by Akita *et al.*[11]. Their complex consists of phenylboronic acid and a phenyl nitronyl nitroxide, which are joined by hydrogen bonds to form alternating 1-D chains. The hydrogen bond is claimed to have an important role on the propagation of ferromagnetic interactions.

Hydrogen-Bonded Radical with Twisted 1-D Chain Structure

The hydrogen-bonded chain structure of **2** is shown in Figure 2. The structure involves an O–H···O type of intermolecular hydrogen bonds between the NO groups of the radical and the OH group of the adjacent molecule, forming a head-to- tail chain structure. The intermolecular O–H···O distance is 2.72 Å, which is comparable to those in other phenol-substituted radicals[3,4]. The N–O groups of the neighboring molecules show dimerized arrangements, with short distances of 3.62 and 3.71 Å for N···O and O···O, respectively. Thus it is expected that antiferromagnetic interactions will predominate in this crystal, due to the presence of the short interatomic distances between the radical molecules.

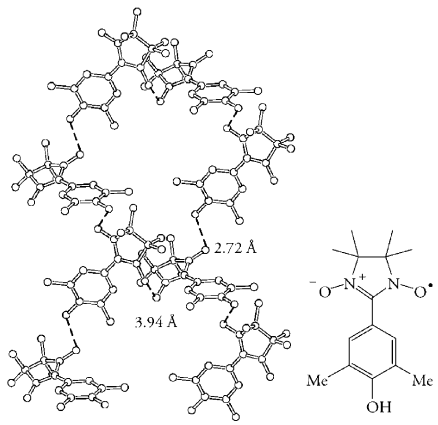

FIGURE 2. 1-D hydrogen-bonded structure in **2**.

Hydrogen-Bonded Radical with Zigzag 1-D Chain Structure

We prepared a pyridone-substituted radical **3** (Figure 3), because the pyridone derivatives are known to form interesting aggregated structure through hydrogen bonds[12]. In the solid state, the molecule of **3** shows a zigzag 1-D chain structure (Figure 3), formed by a strong N–H···O intermolecular hydrogen-bond between the carbonyl oxygen and the

N–H hydrogen of the neighboring molecule. The hydrogen bond distance is 2.676(6) Å, which is significantly shorter than those usually found in 2-pyridone derivatives[13]. Short intermolecular NO···ON distances are found between the chains, and the radical moieties show dimerized arrangements.

The magnetic susceptibility χ_m showed a gradual increase with decreasing temperature, with a maximum at 8 K. Based on the dimer structure described above, the magnetic data were analyzed in terms of an S–T model[14]. The best-fit parameters were $J/k_B = -6.23$ K and $\theta = -0.61$ K.

The reaction of phanolate anions of **2** and **3** with transition metal salts resulted in the formation of only tarry materials, while the reaction of **3** with $M(hfac)_2$ afforded a crystalline complex represented as $M(hfac)_2(PyrNN)_2$[15]. Detailed characterization of these complexes are underway in these laboratories.

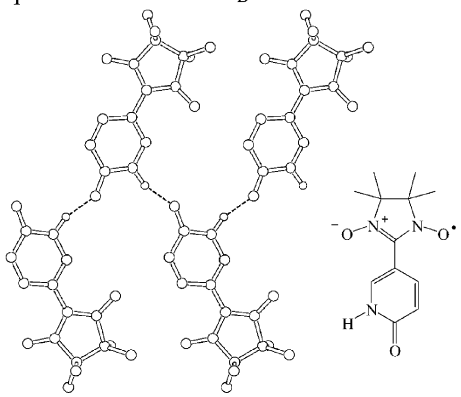

FIGURE 3. X-ray structure of the 1-D hydrogen-bonded chain in **3**.

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