Stable Iminonitroxide Biradical in the Triplet Ground State

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Magnetic properties and crystal structure of a pyridine-substituted iminonitroxide biradical, 2,6-bis(4,4,5,5,-tetramethyl-4,5-dihydro-1*H*-imidazol-2-yl-1-oxyl)pyridine (**1**), were examined. The molecular ground state of **1** was found to be triplet ($S = 1$) with a singlet–triplet energy gap of 7 K. The ground-state triplet biradical serves as a building block for molecule-based magnets of $S > 1/2$ based on intermolecular noncovalent bonding architecture.

The last decades witnessed a rapid development of molecule-based magnetism and spin chemistry.[1] Magnetic properties of molecular assemblages are governed by molecular packing or relative arrangement of open-shell molecules in a crystalline solid state. Some purposive molecular designing is necessary for controlling the molecular packing contributing to intermolecular magnetic interactions.

Noncovalnet bonding such as hydrogen bonding and Coulombic interaction between ionic charges can be a driving force for crystallization of open-shell molecules in a controllable manner.[2] Stable radicals with the ground-state spin quantum number of $S > 1/2$ possessing noncovalent-bonding substituents are sought, from the viewpoint of crystal engineering, for new functionalized open-shell systems such as molecule-based ferrimagnets.[3]

For molecule-based magnets consisting of $S > 1/2$ with intermolecular noncovalent bondings, a 2,6-pyridine-substituted iminonitroxide biradical, 2,6-bis(4,4,5,5,-tetramethyl-4,5-dihydro-1*H*-imidazol-2-yl-1-oxyl)pyridine (**1**), is a promising building block: The neutral molecule **1** can be a hydrogen acceptor. Furthermore, the molecule **1** affords a cationic species with $S = 1$ on N-alkylation of the pyridine ring. Since the biradical **1** was first synthesized,[4] it has been used only as a ligand for transition-metal complexes.[5] In this letter, we report the X-ray crystal structure and magnetic susceptibility of the pristine, metal-free state of **1**, showing that **1** serves for a possible building block for supramolecular magnetics.

The biradical **1** was synthesized by the reported method.[4] In Figure 1 is depicted the molecular structure of **1**.[6] The molecule has a positional disorder of carbon atoms in the tetramethylethylene moiety. The ONCN planes (IM1, IM2) and the pyridine ring (PY) have large dihedral angles (57.83° and 52.91°), which are expected to reduce the π-conjugation and to weaken the intramolecular exchange interaction.

Intermolecular short distances are found at O1–H2 (2.502 Å) and O2–H1 (2.512 Å) between the molecules neighboring along the *b* axis, as depicted in Figure 2. It was found from molecular orbital calculations that large spin densities are distributed on the two iminonitroxide moieties including O1 and O2.[7] Thus, the intermolecular contacts form a spin chain along the *b* axis.

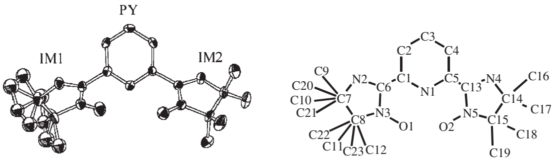

Figure 1. ORTEP drawing of **1** with 50% thermal ellipsoids and the atom numbering. The hydrogen atoms are omitted for clarity.

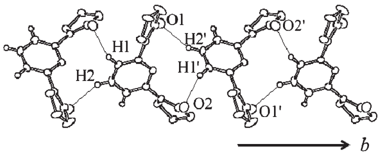

Figure 2. Molecular chain of **1** along the *b* axis. The thin solid lines represent the intermolecular short contacts. The methyl groups are omitted for clarity.

The intramolecular exchange interaction in **1** was examined by paramagnetic susceptibility χ_p for the sample dispersed in a PVC (polyvinylchloride) film,[8] in which intermolecular magnetic interactions are suppressed. The $\chi_p T$ value of the magnetically diluted system increases as the temperature is lowered, as shown in Figure 3. This indicates the occurrence of ferromagnetic interaction within the molecule. The temperature dependence of $\chi_p T$ is analyzed with the Bleany–Bowers model[9]

$$\chi_p = 2\alpha N_A g^2 \mu_B^2 / \{k_B T[3 + \exp(-2J_{FM}/k_B T)]\} \qquad (1)$$

where the parameter J_{FM} represents the intramolecular ferromagnetic exchange interaction and α denotes the purity. The other symbols have their usual meanings. The observed $\chi_p T$ was reproduced by Eq 1 with the parameters $2J_{FM}/k_B = 7.0 \pm 2.5$ K and $\alpha = 0.966$.[8] The g-factor is fixed as $g = 2.0065$, which was observed in the ESR spectrum.[10]

The temperature dependence of $\chi_p T$ measured for neat polycrystalline solid samples of **1** is compared with that of the diluted sample in Figure 3. The $\chi_p T$ value of the neat crystals exhibits a monotonic decrease on lowering the temperature, indicating that antiferromagnetic interactions dominate between the molecules in the crystal. The antiferromagnetic interaction is attributed to the short contacts at O1–H2 and O2–H1 between the molecules along the *b* axis as described above. The antiferromagnetic interaction J_{AF} between the triplet molecules is estimated by using an antiferromagnetic chain model of arbitrary spin S,[11]

$$\chi_p = f[2N_A g^2 \mu_B^2/(3k_B T)][(1+u)(1-u)], \qquad (2a)$$

$$u = \coth[2J_{AF}S(S+1)/(k_B T)] - k_B T/[2J_{AF}S(S+1)], \qquad (2b)$$

$$f = 3/[3 + \exp(-2J_{FM}/k_B T)]. \qquad (2c)$$

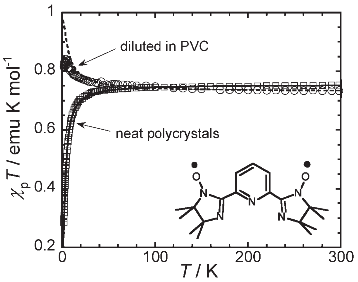

Figure 3. Temperature dependence of paramagnetic susceptibility χ_p of **1** measured on a SQUID magnetometer with $B = 0.1$ T in the $\chi_p T$ vs T plots. The circles represent the $\chi_p T$ values measured for the samples diluted in a PVC film. The dashed lines denote the calculated values from Eq 1. The squares are the $\chi_p T$ values of neat polycrystals. The solid line shows the simulation with Eq 2.

where the spin quantum number is set as $S = 1$. The temperature-dependent density, or the population f, of the triplet state in the molecule **1** is approximated by the simple Boltzmann distribution in Eq 2c. The intermolecular antiferromagnetic interaction was estimated to be $2J_{AF}/k_B = -2.30 \pm 0.05$ K.[12] The model of Eq 2 is based on classical spin approximation.[11] The amplitude of J_{AF} is close to that of J_{FM} which is introduced in the phenomenological way of the Boltzmann distribution. From these, the $2J_{AF}$ value of -2.3 K is only an estimate for the intermolecular interaction.

The amplitude of J_{FM} for **1** is the smallest as compared with those of 2,6-pyridine and *m*-phenylene derivatives of imino- and nitronylnitroxide biradicals.[13] The small interaction in **1** is partly attributed to the weakened π conjugation due to the large dihedral angle between the pyridine and the ONCN groups. The triplet ground state, however, observed in **1** gives us a building block suitable for supramolecular magnets of $S > 1/2$ based on intermolecular noncovalent-bonding architecture.

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References and Notes

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6 Single crystals of **1** were obtained by recrystallization from acetone/cyclohexane solutions. Crystallographic data: $C_{19}H_{27}N_5O_2$, $M_r = 357.45$, Mo Kα, $T = 193$ K, orthorhombic, *Pbca*, $a = 10.320(1)$, $b = 11.9693(8)$, $c = 31.128(3)$ Å, $V = 3845.0(6)$ Å^3, $Z = 8$, $D_{calcd} = 1.235$ g cm^{-3}, 4372 reflections measured, $R = 0.115$, $R_w = 0.2030$ (GOF = 1.0001) for 2537 unique reflections ($I > 2\sigma(I)$) and 250 parameters. The large R value results from the disorder as described in the text. The occupancies of the disordered carbon atoms are optimized in two conformations: C9/C20 = 0.68/0.32, C10/C21 = 0.59/0.41, C11/C22 = 0.68/0.32, C12/C23 = 0.66/0.34.

7 The spin density distribution of **1** in the triplet state was calculated with the unrestricted density functional theory at the UB3LYP/6-31+G(d,p) level using a program package Gaussian 98. The molecular geometry was taken from the X-ray crystal structure. M. J. Frisch, et al, "Gaussian 98, Revision A.9," Gaussian, Inc., Pittsburgh PA (1998).

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12 The intramolecular ferromagnetic interaction and the g-factor were fixed as $2J_{FM}/k_B = 7.0$ K and $g = 2.0065$, respectively. The purity was found to be 100%. It is plausible that the intramolecular interaction J_{FM} in the crystalline solid state is different from that in the PVC film. The interaction J_{FM} was, however, kept unchanged in the simulation with Eq 2 in order to avoid overparameterization.

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