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INTENTIONAL SYNTHESIS OF BINARY RADICAL THAT BEARING NITRONYL AND IMINO NITROXIDES: X-RAY ANALYSIS AND MAGNETIC MEASUREMENT

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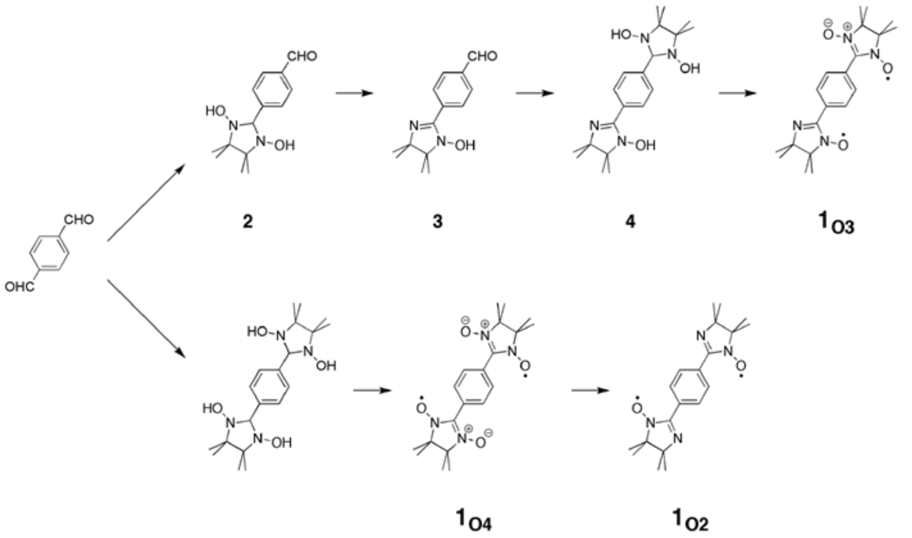
Abstract – We have synthesized new binary radical that bearing both nitronyl and imino nitroxides with the aim of enabling to control the occupancy of oxygen atom in the nitronyl nitroxide crystal. X-Ray analysis, ESR study and magnetic measurement revealed that the tuning of occupancy of the oxygen atom in the crystal might make an effect on the magnetic property of nitronyl nitroxides.

INTRODUCTION

To date nitronyl nitroxides and imino nitroxides have been received much attention because of their stabilities and conveniences of the preparations and applications.[1,2] The nitronyl nitroxide derivatives are usually synthesized in two steps from aldehydes and 2,3-bis(hydroxyamino)-2,3-dimethylbutane. The first step is the cyclization reaction to form imidazolidine ring of precursor that followed by the oxidation reaction to give nitronyl nitroxides. When using bis-aldehyde as the starting reactant, bis(nitronyl nitroxide) radicals can be obtained. The series of imino nitroxides are easily prepared by treatment of related nitronyl nitroxides with nitrogen oxide. During the workup of the oxidation reaction of bis(nitronyl nitroxide) precursor, the minor product as well as target biradical is sometimes separated out. This minor product is a binary radical that bearing both nitronyl and imino nitroxide substituents. There are many experimental and theoretical studies on bis(nitronyl nitroxide) and/or bis(imino nitroxide) molecules,[1,2] but limited papers have described about binary radicals consists of both nitronyl and imino nitroxides.[1,3,4] The intermolecular magnetic interaction is very significant factor for the magnetism of the molecular crystals. The magnetic property of the crystalline sample of nitroxide-based radical is sometimes determined by the intermolecular magnetic interaction that closely related to the stacking pattern of neighboring N-O parts. We addressed our attention to the intentional synthesis of binary radical with the aim of enabling to control the oxygen atom occupancy, and expected to find a difference in the magnetic property of nitronyl nitroxide crystal. To our knowledge, only Turek and co-workers reported the magnetic properties of binary radicals that bearing nitronyl and imino nitroxides in detail,[4] but those radicals are recognized as unexpected side products even in their reports. In this paper, we would like to fix our attention on the intentional synthesis, structural and magnetic studies of binary radical $\mathbf{1_{O3}}$ (Scheme 1).

RESULTS AND DISCUSSION



Scheme 1. Stepwise cyclization to obtain $\mathbf{1_{O3}}$ (above) and simultaneous cyclization for $\mathbf{1_{O2}}$ and $\mathbf{1_{O4}}$ (bottom)

Binary radical $\mathbf{1_{O3}}$ was synthesized by stepwise cyclization method as shown in Scheme 1 (Details are in Experimental section). Structures and abbreviations of reference biradicals ($\mathbf{1_{O2}}$ and $\mathbf{1_{O4}}$) that obtained by simultaneous cyclization reaction are also depicted in Scheme 1. The absorption spectra of $CHCl_3$ solution of three biradicals ($\mathbf{1_{O2}}$, $\mathbf{1_{O3}}$ and $\mathbf{1_{O4}}$) are shown in Figure 1. For $\mathbf{1_{O4}}$ and $\mathbf{1_{O2}}$, typical absorption maxima of nitronyl nitroxide ($\lambda_{max} \approx 610$ nm) and imino nitroxide ($\lambda_{max} \approx 450$ nm) were observed. In contrast, spectrum of $\mathbf{1_{O3}}$ shows broad absorption band in visible range without clear absorption maximum. Owing to this broad absorption band, the color of the solution of $\mathbf{1_{O3}}$ is black, while those of $\mathbf{1_{O2}}$ and $\mathbf{1_{O4}}$ are orange and blue. The existence of two isosbestic points at 410 and 530 nm indicates that the electronic states of two radical substituents in $\mathbf{1_{O3}}$ are independent of each other. ESR spectrum of the toluene solution of $\mathbf{1_{O3}}$ (1.7×10^{-4} M) that degassed by freeze-pump-thaw cycle was measured at room temperature. The observed and simulated ESR spectra are shown in Figure 2. Taking into account of hyperfine coupling of four nitrogen atoms of nitronyl nitroxide and imino nitroxide, observed

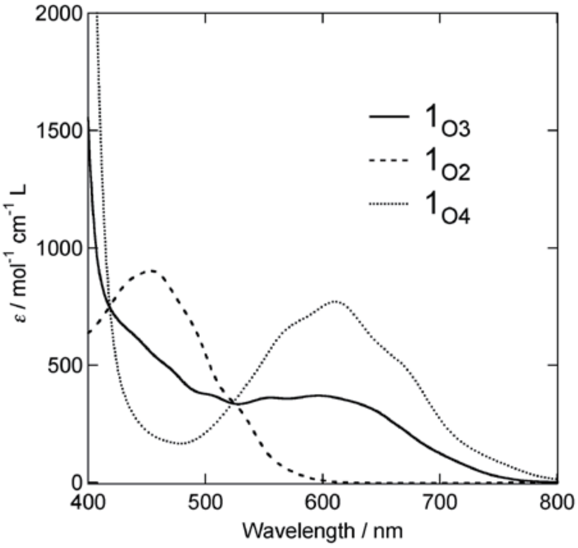


Figure 1. Absorption spectra

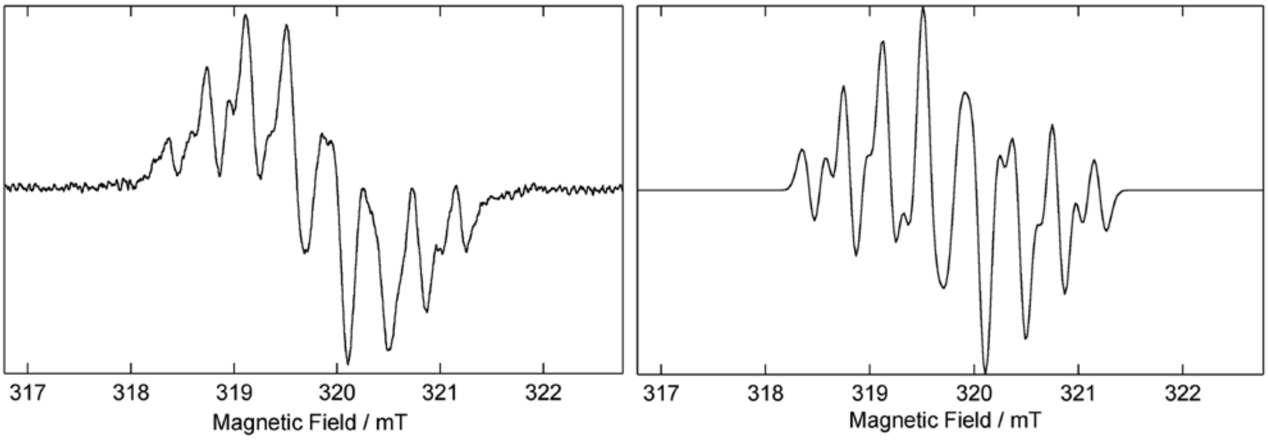


Figure 2. Observed (left) and simulated (right) ESR spectra

spectrum was reproduced by using hyperfine coupling constants of a_{N1} = a_{N2} = 0.367 mT (nitronyl nitroxide fragment), a_{N3} = 0.450 mT and a_{N4} = 0.208 mT (imino nitroxide fragment).

X-Ray crystallographic analyses of three radicals were carried out at 200 K.[5(a)] Although the crystallographic data of **1**$_{O4}$ has already reported,[7] we individually measured its crystal structure to make better condition of comparison of the parameters. Unexpectedly, the crystallographic data of **1**$_{O2}$ has not been reported, and therefore we prepared the single crystal and determined the crystal structure. Their cell parameters are listed in Table 1, and the molecular structure of **1**$_{O3}$ is shown in Figure 3.

Table 1. Cell parameters of three radicals measured at 200 K.

	1$_{O2}$	**1**$_{O3}$	**1**$_{O4}$
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/c$
a / Å	6.9928(15)	6.2176(8)	6.2104(13)
b / Å	14.341(3)	11.5828(16)	11.774(3)
c / Å	9.670(2)	13.8585(19)	13.787(3)
β / deg.	97.468(5)	94.011(3)	92.912(5)
V / Å^3	961.5(3)	995.6(2)	1006.8(4)

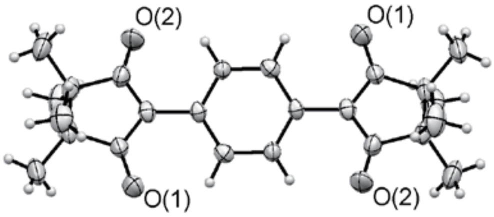


Figure 3. Molecular structure of **1**$_{O3}$. Occupancies are described in the text

All biradical molecules have symmetry centers in the crystals. The cell parameters of **1**$_{O3}$ are similar to those of **1**$_{O4}$ rather than **1**$_{O2}$. The crystal packing manner of **1**$_{O3}$ seems to identical with that of **1**$_{O4}$, but the occupancy of the oxygen atom is very different from each other. Of course, the occupancies of all oxygen atoms in **1**$_{O4}$ are unity, but those found in **1**$_{O3}$ by least square refinement are 0.944(6) for O(1) and 0.568(6) for O(2), respectively. Based on this result, the sum of oxygen occupancies par one molecule of $\mathbf{1_{O3}}$ determined to 3.02. This value is consistent with the molecular structure of $\mathbf{1_{O3}}$.

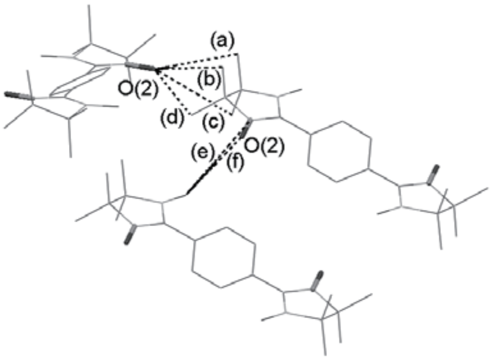


Figure 4. Intermolecular short contacts. Distances (Å) are (a) 3.45, (b) 4.36, (c) 3.62, (d) 3.36, (e) 4.68, (f) 4.77

Torsion angles between the mean planes of *p*-phenylene and imidazoline rings are 17.8° ($\mathbf{1_{O2}}$), 33.3° ($\mathbf{1_{O3}}$) and 33.4° ($\mathbf{1_{O4}}$), respectively. Surprisingly, the torsion angle found in $\mathbf{1_{O3}}$ is almost identical to that of $\mathbf{1_{O4}}$ in spite of the difference in the oxygen occupancies. This result predicts that the intramolecular magnetic exchange of $\mathbf{1_{O3}}$ and $\mathbf{1_{O4}}$ would be similar magnitude.[2c] The short contact distances between O(2) and intermolecular neighboring heterocycles are shown in Figure 4. This X-ray result of intermolecular contact led us to expect to find a difference in the intermolecular magnetic interaction. Additionally, we have succeeded in determining unambiguous molecular structure of $\mathbf{1_{O3}}$ with the aid of the coordination compound. Bis(hexafluoroacetylacetonato)-manganese(II) complex of $\mathbf{1_{O3}}$ was prepared[6] for unambiguous analysis of the molecular structure and the X-Ray result is shown in Figure 5. Unlike the authentic biradical, no disorder of oxygen atom was found in Mn(II) complex. The coordination bond was formed between Mn(II) and oxygen of nitronyl nitroxide, not imino nitroxide fragment.[5b]

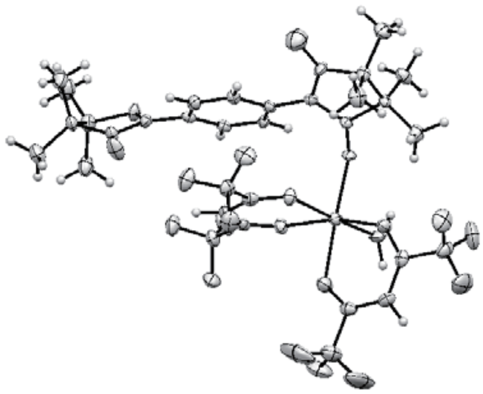


Figure 5. Mn complex of $\mathbf{1_{O3}}$

The magnetic moment of crystalline $\mathbf{1_{O3}}$ was recorded in 0.5 T of applied magnetic field by using SQUID magnetometer. The temperature dependence of magnetic susceptibility (χ_m) and $\chi_m T$ was depicted in Figure 6. As decreasing temperature, $\chi_m T$ value gradually decreased and approached to zero. This behavior indicates that antiferromagnetic magnetic interaction is predominant in the crystal of $\mathbf{1_{O3}}$. Upon cooling the temperature, χ_m increased and reached maximum at 32 K, then recorded a minimum at 6 K and turned to rising again. The theoretical fitting of $\chi_m T$ curve by using of Bleaney-Bowers model revealed that there is exchange interaction of $J/k_B = -26$ K (for $\boldsymbol{H} = -2J\, S_1 S_2$). This result is very different from that of $\mathbf{1_{O4}}$ reported by Gatteschi and his coworkers.[7] In their report, χ_m of $\mathbf{1_{O4}}$ goes through a maximum at 65 K. Although the X-ray result predicted that the intramolecular exchange interaction of $\mathbf{1_{O3}}$ and $\mathbf{1_{O4}}$ would be similar, the magnetic measurement revealed that J/k_B found in $\mathbf{1_{O3}}$ is almost half of the reported value[7] of $\mathbf{1_{O4}}$. Our result revealed that the tuning of the occupancy of oxygen atom in nitronyl nitroxide crystal make an effect on the magnetic properties in low temperature region.

In conclusion, we have successfully synthesized nitronyl and imino nitroxide binary biradical. The oxygen occupancies in the crystal of $\mathbf{1_{O3}}$ were determined to 0.944 and 0.568 by X-ray study. The lowered occupancy of oxygen atom in nitronyl nitroxide affected magnetic behavior of biradical crystal. Our result revealed that the occupancy control of oxygen in nitronyl nitroxide gives a remarkable difference in the magnetic property. It seems like an important clue to designing and tuning the intermolecular magnetic interaction of nitroxide radicals.

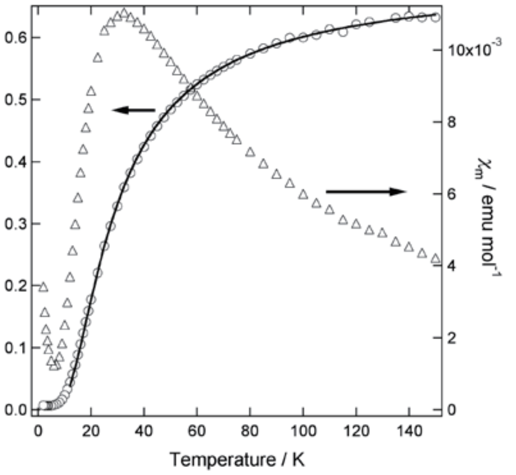


Figure 6. Magnetic property of $\mathbf{1_{O3}}$

EXPERIMENTAL

Synthesis of 2: 1.48 g (10 mmol) of 2,3-bis(hydroxyamino)-2,3-dimethylbutane and 4.82 g (36 mmol) of terephthalaldehyde was dissolved in 230 mL of benzene and refluxed 3 h. The solution was cooled to room temperature and precipitation was filtered off, then dried under reduced pressure. 920 mg of **2** (34.8%) was obtained as white powder. ^{1}H NMR (270 MHz, DMSO-d_6) δ (ppm): 1.06-1.09 (*d*, 12H), 4.60 (*s*, 1H), 7.36-7.90 (*dd*, 4H), 10.01 (*s*, 1H).

Synthesis of 3: To the solution of 529 mg (2.0 mmol) of **2** in 30 mL of MeOH, SeO_2 (22mg, 0.2 mmol) was added and refluxed 1.5 h. The solution was cooled, then filtered through the Celite filter and the filtrate was evaporated under reduced pressure. After the silica-gel column chromatography (R_f = 0.57, $CHCl_3$:MeOH = 7:1), 326 g of **3** (66.1 %) was obtained. ^{1}H NMR (270 MHz, DMSO-d_6) δ (ppm): 1.14 (*br*, 12H), 7.93-7.96 (*d*, 4H), 10.04 (*s*, 1H).

Synthesis of 4: In 7 mL of MeOH, 150 mg (0.61 mmol) of **3** and 108 mg (0.73 mmol) of 2,3-bis(hydroxyamino)-2,3-dimethylbutane were dissolved and refluxed 1 day. The solvent was removed under reduced pressure and the residue was treated by silica-gel column chromatography (R_f = 0.60, $CHCl_3$:MeOH = 3:1). White solid of radical precursor, **4** was obtained (121 mg, 52.9%). ^{1}H NMR (270 MHz, DMSO-d_6) δ (ppm): 0.98-1.24 (*m*, 24H), 4.55 (*s*, 1H), 7.50-7.89 (*d*, *br*, 4H).

Synthesis of $\mathbf{1_{O3}}$: To the ice-cooled $CHCl_3$ (10 mL) solution of **4** (50.0 mg, 0.13 mmol), aqueous $NaIO_4$ (83 mg, 0.39 mmol) was added and stirred 1 h at 0 ˚C. After the usual workup, crude product was purified by silica-gel column chromatography (R_f = 0.37, $CHCl_3$:MeOH = 20:1) and black solid of biradical $\mathbf{1_{O3}}$ (29 mg, 60.6%) was obtained. IR(KBr): ν(N-O) = 1363 cm^{-1}.

Preparation of single crystals: An X-ray-quality single crystal was prepared by recrystallization. The vapor of *n*-hexane was slowly introduced into $CHCl_3$ solution of $\mathbf{1_{O3}}$ and black block crystal of $\mathbf{1_{O3}}$ was obtained after 2 days. Other reference radicals, $\mathbf{1_{O2}}$ (imino nitroxide biradical) and $\mathbf{1_{O4}}$ (nitronyl nitroxide biradical) were also synthesized by the methods similar to those in literatures.[1,7] The single crystals of $\mathbf{1_{O2}}$ and $\mathbf{1_{O4}}$ are prepared by similar procedure to that used for $\mathbf{1_{O3}}$. For the recrystallization of $\mathbf{1_{O2}}$, *n*-pentane was used as poor solvent instead of *n*-hexane.

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6. The complex was synthesized by the reaction between equimolar of $\mathbf{1_{O3}}$/$CHCl_3$ and bis(hexafluoroacetylacetonato)manganese(II)/*n*-heptane. The solution was kept standing and deep-green single crystal of the complex was precipitated out within a day.
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