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Synthesis and Magnetic Properties of Dimethylmethylenebis(iminonitroxide) Diradical

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Dimethylmethylenebis(iminonitroxide) diradical **1** was prepared from 3-hydroxy-2,2-dimethylpropanal in five steps. The structure, ESR spectrum, and magnetic properties are reported: **1** exhibited an antiferromagnetic interaction of $J/k_B = -72\,K$ ($\boldsymbol{H} = -2J\mathbf{S}_1\cdot\mathbf{S}_2$).

The synthesis and characterization of new high-spin molecules are important subjects in the field of molecule-based magnets,[1] in which the exchange interaction between the spin centers plays an important role in determining the bulk magnetic properties.[2] The sign of intramolecular exchange interaction can be predicted by a simple π-topology rule[3] in some cases. However, such a prediction is difficult for σ-frame-spaced diradical systems. Generally speaking, the exchange interaction is conformation-dependent. The dependence of the exchange interaction on the torsion angle (between the spacer and spin sources) for *m*-phenylene- and/or alkylidene-spaced diradicals is well documented.[4,5] There have been very few studies on sp^3-C-spaced biradicals.[6]

Methylenebis(nitronylnitroxide) and -(iminonitroxide) are interesting biradicals in this context: The exchange interaction between the two nitroxide spins can be strongly dependent on the conformation. Theoretical calculations were carried out for two conformations **I** and **II** of dimethylmethylenebis(iminonitroxide) diradical **1** (Chart 1). Conformer **I** has two spin centers in the vicinity with an O–O distance of 3.49 Å and a dihedral angle (between the two iminonitroxide-planes defined by N=C–N–O) of ca. 75° (vide infra). In conformer **II**, two iminonitroxides are nearly coplanar with a O–O distance of 5.51 Å.[7,8] Conformer **II** has a higher energy level than the conformer **I** because of the steric repulsion between the oxygen atoms and the methyl groups on the methylene-carbon atom (Supporting Information).[9] However, conformer **II** should take a predominant role when ligated to a Lewis acid including a magnetic metal ion. The formation of this type of complex has been observed in the reaction of the related dimethylmethylenebis(4,5-dihydro-1,3-oxazole)s with Cu(II) ions.[10] The calculated exchange interactions are antiferromagnetic ($\boldsymbol{H} = -2J\mathbf{S}_1\cdot\mathbf{S}_2$, $J/k_B \approx -89\,K$) for conformer **I** and ferromagnetic ($J/k_B \approx +34\,K$) for conformer **II** (Supporting Information).[9,11,12] Experimental studies for methylenebis(nitronylnitroxide) and -(iminonitroxide) have thus far not been reported: this is probably because of the difficulty in the double condensation step of bisaldehyde (or bisacetal) with 2,3-di(hydroxyamino)-2,3-dimethylbutane. For the synthesis of the target biradicals, stepwise introduction of the stable radicals seems to be essential. We report the synthesis, structure, ESR spectrum, and magnetic properties of **1**.

1 was prepared from 3-hydroxy-2,2-dimethylpropanal (**2**) in five steps (Scheme 1).[9] Condensation of **2** with 2,3-diamino-2,3-dimethylbutane (**3**) gave **4**. *m*-CPBA and $NaIO_4$ oxidation[13] of aminal **4**, followed by treatment with $NaNO_2$–CH_3CO_2H gave iminonitroxide-alcohol **5**. The oxidation of **5** requires mild conditions. We found that the iminonitroxide moiety was stable under the Swern oxidation conditions, giving key intermediate **6**. Repeating similar procedures from **2** to **5** gave **1** as red prisms, which was stable under aerated conditions.

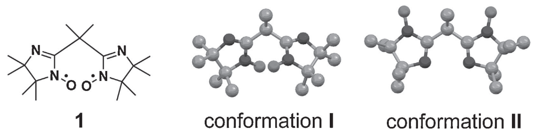
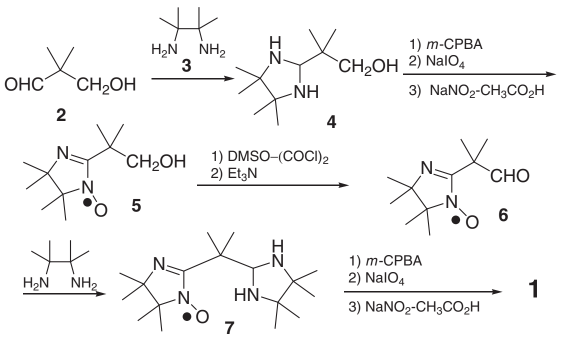

1　conformation **I**　conformation **II**

Chart 1.



Scheme 1.

The X-ray crystal structure of **1** is shown in Figure 1.[14] **1** has a C_2-symmetry. The dihedral angle between the plane (O1–N1–C1=N2) and the plane (O1*–N1*–C1*=N2*) is ca. 75°. The distance between the two oxygen atoms (O1 and O1*) is 3.49 Å, which is longer than that of the sum of van der Waals radii of oxygen atoms (ca. 3.0 Å). There are no intermolecular contacts between the spin centers (C1, N1, N2, and O1 atoms) within the sum of van der Waals radii.

Figure 2 shows the ESR spectrum of **1** in a frozen diethyl phthalate matrix at 200 K. Fine-structured triplet-state ESR signals ($\Delta m_s = \pm1$) were clearly observed in addition to the central signals due to monoradical impurities. The high-spin nature of the main signals is also supported by the observation of weak forbidden signal ($\Delta m_s = \pm2$) in a half-field region. A spectral simulation yielded the following spin Hamiltonian parameters for the $S = 1$ state: $|D|/hc = 0.0412\,\mathrm{cm}^{-1}$, $|E|/hc = 0.0044\,\mathrm{cm}^{-1}$, $g_{XX} = 2.0081$, $g_{YY} = 2.0052$, and $g_{ZZ} = 2.0031$. The large *D*-value is compatible with the structure of conformation **I**.

The plots of the ESR signal intensity ($\Delta m_s = \pm2$) vs. reciprocal temperature showed a convex curve with a maximum

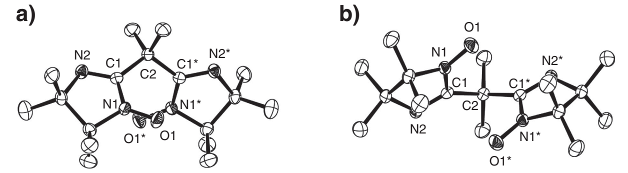


Figure 1. ORTEP view of **1** showing 50% thermal ellipsoids: (a) Top view and (b) side view.

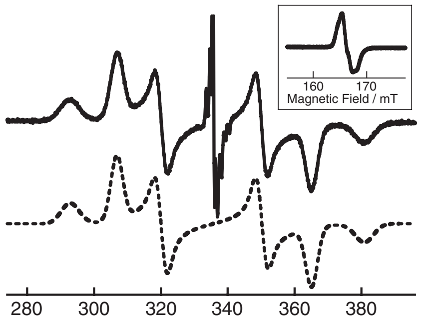


Figure 2. ESR spectrum (solid line) of **1** in diethyl phthalate at 200 K and its simulated spectrum (dashed line). The central sharp signals in the observed spectrum are attributed to a monoradical impurity. Inset: A signal due to the forbidden transition at 200 K.

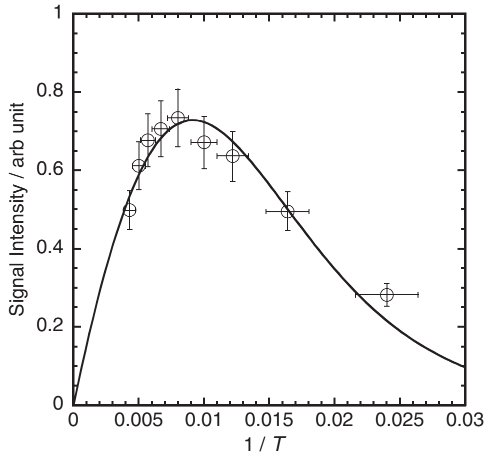


Figure 3. The plots of the signal intensity ($\Delta m_s = \pm 2$) vs. $1/T$. The solid curve is a simulation line based on the S–T model with $J/k_B = -88$ K.

around 110 K (Figure 3). The curve was simulated using the Bleaney–Bowers model (S–T model).[15] The exchange interaction was estimated to be $J/k_B = -88 \pm 3$ K. This value is in good agreement with the theoretical estimation ($J/k_B = -89$ K for conformation **I**, vide supra), suggesting that the conformation in the diethyl phthalate matrix is identical with that in the crystalline state.

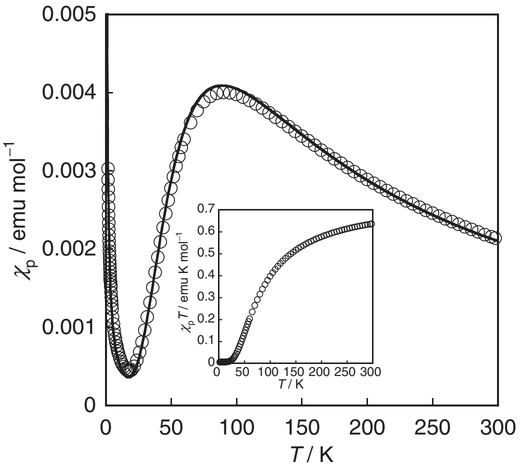


Figure 4. The χ_p–T plots for **1** under an external magnetic field of 0.1 T. The solid line is a simulation curve by the Bleaney–Bowers model using $J/k_B = -72$ K ($\boldsymbol{H} = -2J\mathbf{S}_1\cdot\mathbf{S}_2$, purity: 98.5%). The simulation curve includes monoradical impurity (1.5%). Inset: $\chi_p T$–T plots.

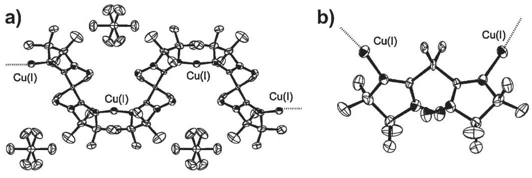


Figure 5. (a) ORTEP view of **1**–CuPF$_6$ complex showing 50% thermal ellipsoids and (b) conformation of **1** within the complex.

Bulk magnetic properties in a polycrystalline state were studied by measuring temperature dependence (1.8–298 K) of the magnetic susceptibility (χ_p) under an external magnetic field of 0.1 T (Figure 4). The $\chi_p T$ value was 0.636 emu K mol^{-1} at room temperature and gradually decreased on lowering the temperature. Furthermore, the χ_p–T plots showed a maximum temperature of ca. 90 K, which was simulated using the Bleaney–Bowers model (eq 1)[15] to give $J/k_B = -72$ K ($\boldsymbol{H} = -2J\mathbf{S}_1\cdot\mathbf{S}_2$, purity: 98.5%; g value: 2.006). This value is close to the exchange interaction in the diethyl phthalate matrix.

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

We have shown that **1** exhibits sizable antiferromagnetic interaction between the two nitroxide spins. Metal complexation may switch the magnetic interaction from antiferro- to ferromagnetic interaction. We have examined the complexation of **1** with Cu ions. Although we have not yet succeeded in obtaining a good crystal for a Cu(II)-complex, we have obtained chain complexes with Cu^{I}PF$_6$ and Cu^{I}Cl salts.[9,16] The structure of the **1**–Cu^{I}PF$_6$ complex is shown in Figure 5; the conformation of **1** within **1**–Cu^{I}PF$_6$ is very similar to conformation **I** (Figure 5b).

The complexation of **1** with magnetic metal ions and the clarification of magnetic properties are in progress.

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References and Notes

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7 The geometry of conformer **I** was taken from the crystal structure of **1**. The structure of conformer **II** was obtained by geometry optimization under the constrained conditions of dihedral angle = 0 between the two nitroxide planes using *Spartan'08*.[8] The triplet and the broken-symmetry singlet states were calculated using *Gaussian 09* program package.[11]

8 *Spartan'08*, Wavefunction, Inc. Irvine, CA.

9 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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