

Magnetic Phase Transition in a Heteromolecular Hydrogen-Bonded Complex of Nitronylnitroxide Radicals

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An organic molecular acid–base complex has been synthesized from pyridine-substituted biradical **2** in a triplet ($S = 1$) ground state and a benzoic acid derivative of monoradical **3** with $S = 1/2$. The two constituent molecules are bound by an OH–N hydrogen bond in a crystalline solid state. The complex has been found to exhibit an antiferromagnetic phase transition at 5 K. The complex is the first example of a hydrogen-bonded heterospin, heteromolecular complex exhibiting a magnetic phase transition in purely organic molecule-based materials.

The past decades have witnessed a rapid development of molecule-based magnetism and spin chemistry.¹ Magnetic properties of open-shell molecular assemblages are governed by molecular packing in crystalline solid states. It has been a challenging issue to make open-shell molecular crystals with desirable molecular packings in a rationalized and controllable manner. The control of crystal structures has been achieved in part by introducing hydrogen-donating and -accepting substituents to stable radicals such as nitronylnitroxide with an unpaired electron spin $S = 1/2$.^{2,3} The success of hydrogen-bonded aggregation is attributed to its directionality and strength as compared with other noncovalent bondings from the viewpoint of crystal engineering.

In this study, we extend the approach of hydrogen-bonded molecular assemblage to two-component aggregation, in which both the components have unpaired electron spins. An OH...N hydrogen bond between carboxylic acid and pyridine is invoked to cocrystallize two inequivalent open-shell molecular entities with different spin quantum numbers S . An organic acid–base complex **1** (Figure 1) has been synthesized, which is composed of a pyridine-substituted biradical **2**⁴ and a benzoic acid derivative of monoradical **3**.⁵ The biradical **2** is known to have a triplet ($S = 1$) ground state.⁶ The complex **1** is the first example of a hydrogen-bonded organic complex composed of inequivalent open-shell constituent molecules. We have examined the X-ray crystallography and the magnetic properties of the complex **1** and found that it exhibits a magnetic phase transition.

The constituent molecules **2** and **3** were synthesized by literature procedures.^{4,5} Single crystals of the complex **1** were obtained by recrystallization from acetone and pentane solutions.

In Figure 1 is depicted the asymmetric unit of the complex **1**.⁷ The biradical **2** and the monoradical **3** are bound by the

OH...N hydrogen bond at O7–N1. The molecules **2** and **3** in the hydrogen-bonded pair are almost coplanar,⁸ and the pairs are π -stacked in the direction nearly perpendicular to the hydrogen bond. The π -stacked molecular packing gives a chain structure along $a + c$, as shown in Figure 2. Intermolecular short distances close to the van der Waals contact⁹ are found within the chain: (i) 2.993(4) Å at O2–C26, (ii) 3.195(4) Å at O3–C26, (iii) 3.293(4) Å at O6–C13, and (iv) 3.600(4) Å at O1–C6.¹⁰ All of the four contacts occur between the 2-positioned, central carbon atom of the nitronylnitroxide group and the nitroxide oxygen atom of the neighboring molecules. The central carbon atom of nitronylnitroxide usually has a negative spin density.¹¹ Intermolecular short contacts between the negatively spin polarized carbon atom and the nitroxide oxygen atom with a large, positive spin density give rise to intermolecular ferromagnetic interactions as found in other nitronylnitroxide crystals.^{5,12} All of the four contacts contribute to possible intermolecular ferromagnetic interactions.

Another short contact is found at the nitroxide oxygen O6 and the phenyl carbon atom C25 of the adjacent molecule (O6–C25 = 3.327(3) Å),¹⁰ as designated (v) in Figure 2. A side-by-side contact between two phenylnitronylnitroxide radical molecules, such as O6–C25, is known to afford intermolecular ferromagnetic interactions.¹³ Thus, all the contacts (i) to (v) in the molecular chain are expected to contribute to intermolecular ferromagnetic interactions.¹⁴ These possible ferromagnetic interactions, together with the intramolecular ferromagnetic interaction in the biradical **2**, afford a ferromagnetic one-dimensional chain arrangement along $a + c$, as depicted in Figure 2b.

The molecular chains are connected with each other by intermolecular short contacts in two directions nearly perpendicular to the chain. One is the OH...N hydrogen bond at O7–N1 as described above, giving the molecular packing of the hydrogen-bonded pairs in the ac plane. Between the neighboring molecular planes is found the other interchain contact at the

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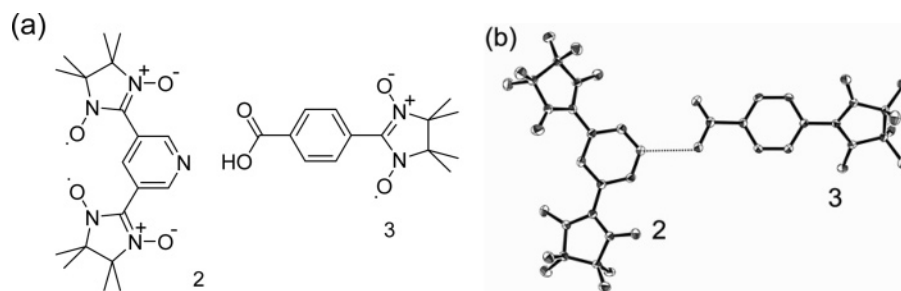


Figure 1. (a) Biradical **2** and monoradical **3**. (b) ORTEP view of complex **1** with the thermal ellipsoids at the 50% probability level. The hydrogen atoms are omitted for clarity. The dashed line represents the hydrogen bond with the O7–N1 distance of 2.656(4) Å.

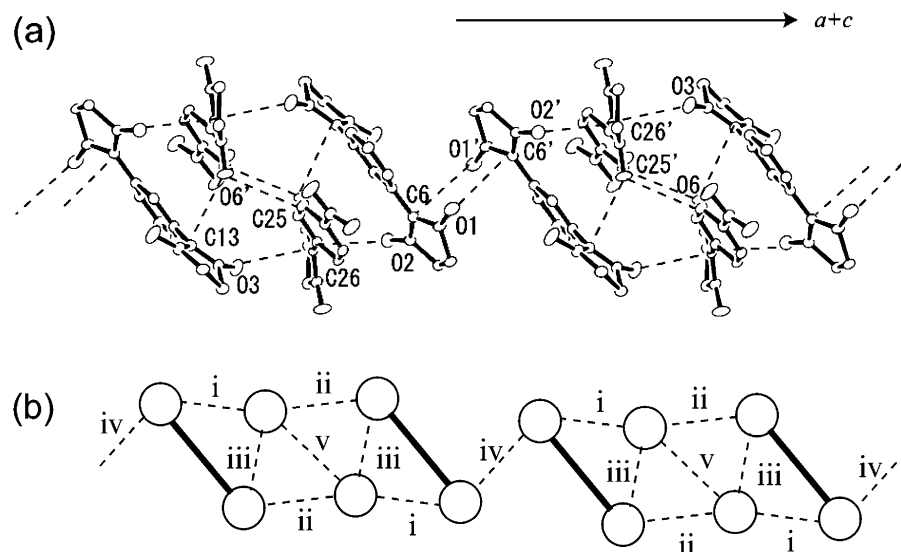


Figure 2. (a) Molecular chain of **1** running along $a + c$. The dashed lines represent the intermolecular short contacts. The methyl groups and the hydrogen atoms are omitted for clarity. (b) Schematic drawing of the exchange coupling in the chain. The circles represent the $S = 1/2$ spins.

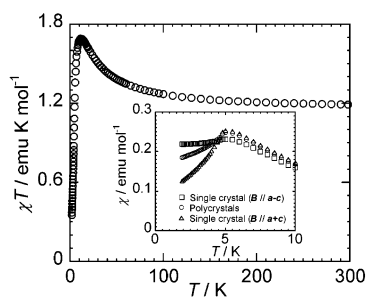


Figure 3. Temperature dependence of magnetic susceptibility χ of **1** measured on a SQUID magnetometer. The circles represent the χT values of the polycrystals under the magnetic field $B = 10$ mT. In the inset are shown the χ values measured for the polycrystals (circles, $B = 10$ mT) and an aligned single crystal (triangles: $B // a + c$, squares: $B // a - c$; $B = 5$ mT).

methyl group (C10) and the nitroxide oxygen atom (O5) (O5–C10 = 3.248(3) Å). The magnetic exchange interactions between the chains should be weak as compared with the intrachain ones, since the pyridine nitrogen atom (N1), the hydroxyl group (O7), and the methyl group (C10) have small spin densities.¹¹

The temperature dependence of the magnetic susceptibility χ of the complex **1** measured for randomly oriented polycrystals is shown in Figure 3 in the χT versus T plots.¹⁵ The χT value increases as the temperature is lowered, showing that ferromagnetic interactions predominate in the crystal. The χT exceeds 1.38 emu K mol^{−1}, which is expected for a pair of an $S = 1$ and an $S = 1/2$ spin. This indicates that the ferromagnetic interactions are propagated between the molecules. The inter-

molecular short contacts (i) to (v) within the chain along $a + c$ should be responsible for the ferromagnetic interactions. The χT value, however, has a maximum at 11 K, indicating the occurrence of additional antiferromagnetic interactions.

The magnetic susceptibility χ measured for the polycrystals exhibits a peak at 5 K, as depicted in the inset of Figure 3, suggesting an antiferromagnetic phase transition with the Néel temperature of $T_N = 5$ K. The susceptibility χ of an aligned single crystal of **1** was measured with an applied magnetic field B in two directions; $B // a - c$ and $B // a + c$.¹⁶ Under the field $B // a - c$, the χ value hardly varies with temperature. The temperature-independent susceptibility is typical of ordered antiferromagnets under an applied field perpendicular to the easily magnetized axis. For $B // a + c$, on the other hand, the χ value is substantially reduced on lowering the temperature.¹⁷ The anisotropy of χ appearing below 5 K confirms the occurrence of an antiferromagnetic phase transition at $T_N = 5$ K in **1**.¹⁸ Magnetization versus magnetic field curves measured below $T_N = 5$ K are S-shaped, which is consistent with the antiferromagnetic ordering of the ferromagnetically aligned spins in the chains.

The complex **1** is the first example of a hydrogen-bonded heterospin, heteromolecular complex exhibiting a magnetic phase transition. The present results indicate that the hydrogen bond between organic acids and bases is an efficient structure-determining factor of forced cocrystallization of open-shell molecules with inequivalent spins, which leads to novel molecule-based magnetic materials such as ferrimagnets.

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Supporting Information Available: Crystallographic data (CIF file) and ORTEP drawings of the complex **1**, magnetic susceptibility data of **2**, and table of atomic spin densities calculated by DFT methods. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References and Notes

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- (6) The magnetic susceptibility of **2** has been reported in ref 4. Only a monotonic decrease in χT on lowering the temperature has been observed for the crystalline solid state owing to intermolecular antiferromagnetic interactions. The intramolecular ferromagnetic interaction (the singlet–triplet energy gap of $2J/k_B \approx 40$ K) of **2** was clarified from susceptibility measurements on a sample dispersed in a polymer film, in which intermolecular magnetic interactions were suppressed. The susceptibility data of **2** in the polymer film is given in Supporting Information.
- (7) The crystal structure was solved by direct methods in a program package *CrystalStructure* (version 3.60) from Rigaku/Molecular Structure Corporation, The Woodlands, TX. Crystallographic data: $C_{33}H_{44}N_7O_8$, $M = 666.75$, $0.30 \times 0.23 \times 0.05$ mm³, Mo K α , 143 K, triclinic, $P\bar{1}$, $a = 11.839(3)$ Å, $b = 12.637(3)$ Å, $c = 12.977(3)$ Å, $\alpha = 96.936(3)^\circ$, $\beta = 100.902(3)^\circ$, $\gamma = 114.716(4)^\circ$, $V = 1687.7(7)$ Å³, $Z = 2$, $D_{\text{calc}} = 1.312$ g cm⁻³, $R = 0.070$, $R_w = 0.268$ optimized on F^2 (GOF = 1.002) for 5957 reflections ($I > 3\sigma(I)$) and 477 parameters.
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- (14) The contact (iv) is accompanied by an inversion-related NO–NO contact with the N–O distance of 3.740(4) Å, which contributes to possible antiferromagnetic interactions due to a direct overlap of singly occupied molecular orbitals. From the experimental data of χ vs T , we are not allowed to discriminate between the N–O contact and the interchain contacts as the origin of the antiferromagnetic interaction contributing to the phase transition.
- (15) The diamagnetic contribution of -450×10^{-6} emu mol⁻¹ was subtracted.
- (16) The accuracy of the alignment of the single crystal was $\pm 5^\circ$ with respect to the direction of the applied magnetic field.
- (17) From mean-field theories of conventional antiferromagnets, the χ value with B parallel to the easily magnetized axis is expected to approach zero. The observed nonvanishing χ for $B/a + c$ in the limit of $T = 0$ is attributed either to the misalignment of the crystal with errors of $\pm 5^\circ$ or to inclination of the easily magnetized axis of **1** from $a + c$.
- (18) A specific heat measured for the polycrystalline samples of complex **1** exhibited a sharp λ -like peak at 4.8 K. The peak was found to shift to lower temperatures upon application of static magnetic fields. These findings confirm the three-dimensional antiferromagnetic phase transition occurring in **1**.