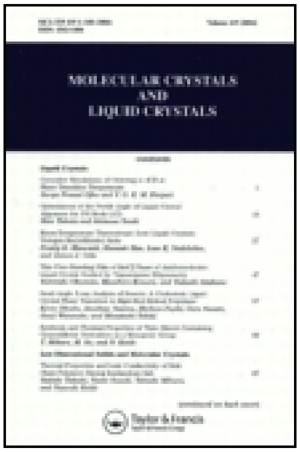

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Intermolecular Spin-Coupler: Ferromagnetic Spin Interactions Through Hydrogen Bond in the Complexes of Arylboronic Acids with Aryl Nitronyl Nitroxides

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INTERMOLECULAR SPIN-COUPLER : FERROMAGNETIC SPIN INTERACTIONS THROUGH HYDROGEN BOND IN THE COMPLEXES OF ARYLBORONIC ACIDS WITH ARYL NITRONYL NITROXIDES

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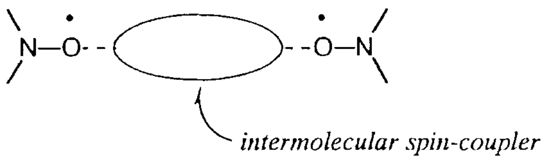
Abstract Two crystalline complexes, the complex of *p*-fluorophenylboronic acid with phenyl nitronyl nitroxide (**2**) and the complex of *p*-nitrophenylboronic acid with *p*-dimethylaminophenyl nitronyl nitroxide (**3**), were prepared. Both of those complexes as well as the complex of phenylboronic acid with phenyl nitronyl nitroxide (**1**) exhibit ferromagnetic spin interactions (**1**: J/k_B=+0.65 K, **2**: J/k_B=+0.58 K, **3**: J/k_B=+1.35 K). The results are discussed based on the X-ray crystal structure.

INTRODUCTION

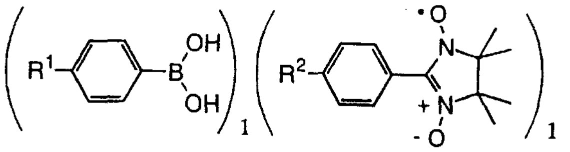
In order to attain a long-range goal of constructing organic ferromagnets, various intramolecular magnetic couplers that connect radical centers ferromagnetically have been proposed and their sign and magnitude of the coupling have been investigated.[1] For the construction of bulk magnetic materials it is further required to develop intermolecular spin couplers. We have recently introduced a new strategy for intermolecular spin couplers in which the spins interact ferromagnetically via hydrogen-bonding;[2] phenylboronic acid, having two OH groups on a boron atom, has been found to provide a direct spin-transmission path way for the nitronyl nitroxide radicals through the NO···HO-B-OH··· ON hydrogen bonds. Thus, complexation of phenylboronic acids with nitroxide radicals are of interest as building-blocks of magnetic materials with supramolecular structure.



In this paper we describe the 1:1 molecular complexes derived from *p*-substituted phenylboronic acids and aryl nitronyl nitroxides and discuss their magnetic properties based on the X-ray crystal structures.

MATERIALS

Two crystalline complexes, one composed of *p*-fluorophenylboronic acid[3] and phenyl nitronyl nitroxide[4] (**2**) and another *p*-nitrophenylboronic acid[5] and *p*-dimethylaminophenyl nitronyl nitroxide[4] (**3**), were prepared. Complex **2** was obtained in good yields as blue prisms by recrystallization of an equimolar mixture of *p*-fluorophenylboronic acid and phenyl nitronyl nitroxide from diethyl ether. The 1:1 stoichiometric ratio of the complex was confirmed based on elemental analysis. In a similar manner, complex **3** with a 1:1 ratio was prepared as dark green needles from a solution of *p*-nitrophenylboronic acid and *p*-dimethylaminophenyl nitronyl nitroxide in a mixed solvent of tetrahydrofuran and hexane. These crystalline complexes are stable at ambient temperature.



1: $R^1 = R^2 = H$
2: $R^1 = F$, $R^2 = H$
3: $R^{1'} = NO_2$, $R^2 = NMe_2$

MAGNETIC PROPERTIES

The magnetic behavior of polycrystalline samples of the complexes was investigated by means of a SQUID susceptometer. Figures 1 and 2 show the temperature dependence of the product of the paramagnetic susceptibility (χ) with the temperature (T). For both complexes, the plot clearly reveals an increase of the χT value with decreasing temperature. The results indicate that the ferromagnetic spin interaction is predominant at low temperature in both **2** and **3**. At temperatures less than 2.6 K, χT of **3** steeply decreases. On the other hand, χT of **2** continues to increase down to 1.8 K. These observations suggest that the weak antiferromagnetic interactions other than ferromagnetic one are involved in the crystal of **3**.

Taking the crystal structure (*vide infra*) into consideration, the experimental data of **2** were rationalized in terms of the one-dimensional Heisenberg model for ferromagnetically coupled linear arrays of spin 1/2.[6] Even though the crystal structure of complex **3** could not be determined because of difficulty in obtaining single crystals suitable for an X-ray analysis, the data of **3** was also analyzed, for comparison, by the same model as used in **2**. Thus, the following expression was used.

$$\chi = (Ng^2\mu_B{}^2/4kT)\left[\frac{(1.0+5.798x+16.903x^2+29.377x^3+29.833x^4+14.037x^5)}{(1.0+2.798x+7.009x^2+8.654x^3+4.574x^4)}\right]^{2/3}$$

where $x = J/2kT$

When the interchain antiferromagnetic interactions (J') are included, the total susceptibility is given by the following expression.

$$\chi_{total} = \chi / [1-2zJ'\chi/(Ng^2\mu_B{}^2)]$$

Fitting the experimental data to these expressions yields the best-fit parameters summarized in Table 1. Because of the weak interaction, the significant error in J value might be involved. However, when we compare the curves of **2** and **3**, the increase of χT values in **3** starts at higher temperature than that of **2** does. Thus, the ferromagnetic interaction in **3** is stronger than that of **2**.

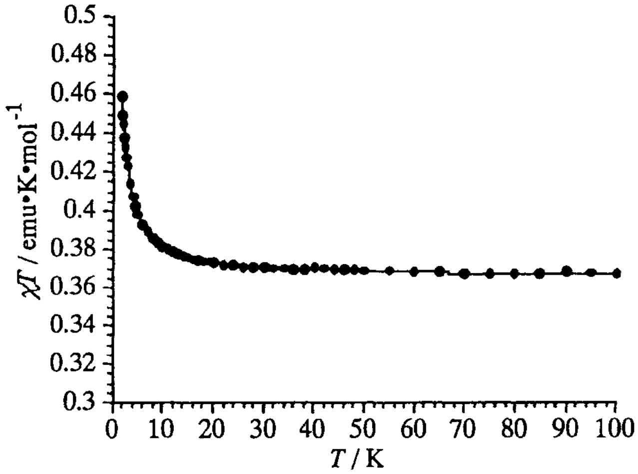


FIGURE 1 Temperature dependence of products of paramagnetic susceptibility and temperature for complex **2**. The solid line is calculated based on the 1-D Heisenberg model.

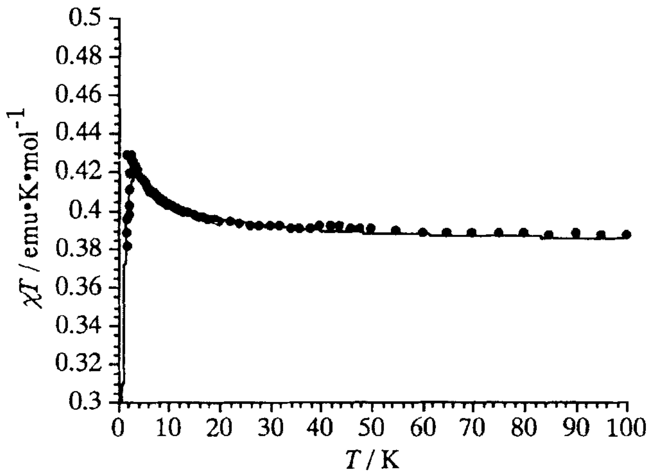


FIGURE 2 Temperature dependence of products of paramagnetic susceptibility and temperature for complex **3**. The solid line is calculated based on the 1-D Heisenberg model.

TABLE 1 Calculated J and J' values obtained by fitting to the 1-D Heisenberg model.

complex	R^1	R^2	J/k_B	J'/k_B
1	**H**	**H**	0.65 K	-0.40 K
2	**F**	**H**	0.58	-0.16
3	**NO_2**	**NMe_2**	1.35	-0.58

CRYSTAL STRUCTURE OF 2

The crystal structure of complex **2** was determined by single crystal X-ray diffraction. Crystal data are as follow; $C_{19}H_{23}BN_2O_4F$, monoclinic, space group $P2_1/n$, a = 13.664(2) Å, b = 9.642(3) Å, c = 14.781(2) Å, β = 90.72(1)°, Z = 4, D_{calc} = 1.275 g•cm^{-1}; 4952 reflections measured; 2695 reflections observed ($F_o > 3\sigma(F_o)$); 314 parameters refined; 2θmax = 55° ; R = 0.048, R_W = 0.057. The asymmetric unit is comprised of one nitronyl nitroxide molecule and one boronic acid molecule. The molecular structure is shown in Figure 3 (two asymmetric units are shown). The boronic acid moiety is trigonal planer and almost coplanar with the substituent phenyl ring, the dihedral angle being about 7°. The π-plane of the nitronyl nitroxide group twists to the phenyl ring with a torsional angle of about 34°. Two hydroxyl groups of the boronic acid are connected to the oxygen atoms of the nitroxide group with the O··O hydrogen-bonding distance of 2.790 Å and 2.807 Å. Thus nitronyl nitroxide molecules are arranged alternately with boronic acid molecules to make an infinite helical chain as shown in Figure 4.

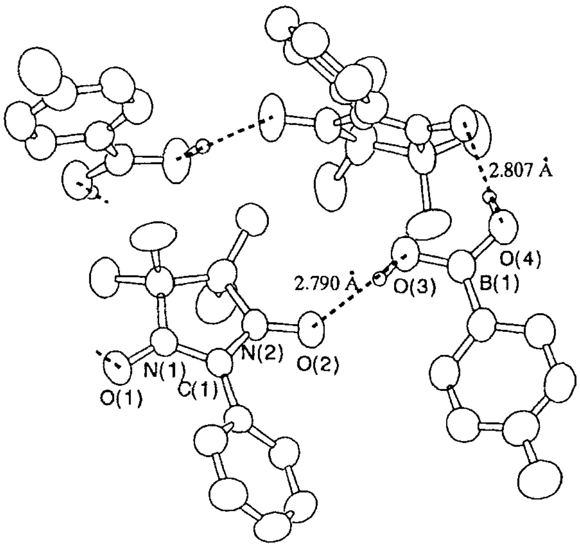


FIGURE 3 Molecular structure of **2**.

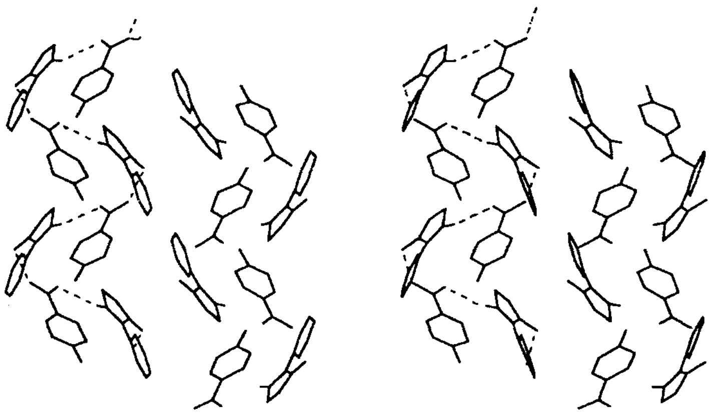


FIGURE 4 Stereoview of the helical chain structure of **2** linked by hydrogen bonds. For simplicity, the hydrogen atoms and methyl groups are not shown.

The molecular structure and the hydrogen bonding pattern of **2** described above are almost similar to those of **1** only with slight difference in hydrogen bond lengths (O··O for **1**: 2.785 Å, 2.792 Å) and interchain arrangement of the nitronyl nitroxide molecules.[2] In the crystal of **2**, two nitroxide molecules in the neighboring helical chain are overlapped pairwise to locate the oxygen atom (O(1)) of the nitroxide molecule close to the C(1) atom of the other nitroxide molecule, as shown in Figure 5. On the other hand, in the crystal of **1**, two molecules are arranged in parallelwise overlapping to locate the oxygen atom on the center of C(1)-N(1) bond of the other molecule, as shown in Figure 6, which is considered to result in weak interchain antiferromagnetic interaction due to a SOMO-SOMO overlap.

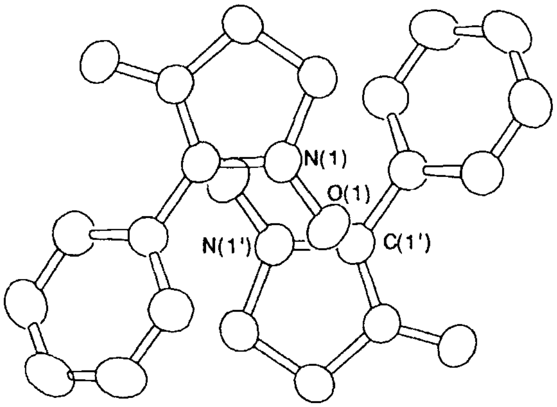


FIGURE 5 Interchain arrangement of nitronyl nitroxide molecule of **2**. For simplicity, the hydrogen atoms and methyl groups are not shown. Selected interatomic distances : O(1)-C(1') ; 4.32 Å, O(1)-N(1') ; 4.39 Å, N(1)-N(1') ; 4.54 Å

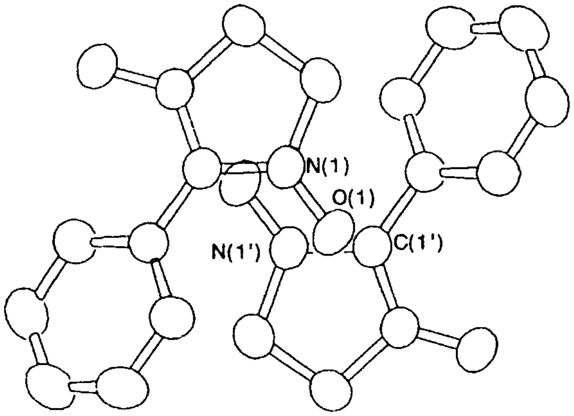


FIGURE 6 Interchain arrangement of nitronyl nitroxide molecule of **1**. For simplicity, the hydrogen atoms and methyl groups are not shown. Selected interatomic distances : O(1)-C(1') ; 4.49 Å, O(1)-N(1') ; 4.50 Å, N(1)-N(1') ; 4.64 Å

DISCUSSION

In a previous report,[2] we have ascribed the ferromagnetic interaction observed in crystals of **1** to the spin transmission path through the NO-HOBOH-ON hydrogen bond. In the present study, we have revealed that both of complexes **1** and **2** have the same hydrogen bond pattern, NO-HOBOH-ON. This linkage is assumed to be responsible for ferromagnetic interaction in **2** as well. The close contacts of two nitroxide moieties in **2** exhibit two modes; one includes contact of the radical center N-O to the C(1) atom on which negative spin density is induced by spin polarization and another makes parallel contact of the N-O groups in head-to-tail manner. The former would make ferromagnetic contribution[7] and the latter antiferromagnetic one[8]. At this stage we cannot determine which is predominant, since the interactions are weak.

In the case of **3**, an electron-withdrawing group substituted on boronic acid and an electron-donating group on nitronyl nitroxide would facilitate interactions between the LUMO of boronic acid and the SOMO of nitronyl nitroxide. Therefore, significant electronic and steric effects appear to be included in the spin-interaction of **3**.

Complexation with diamagnetic organic molecule such as boronic acids may generally be considered to result in the dilution of the spin concentration in the solid-state and therefore seems to be not promising from the viewpoint of spin-interaction. Nevertheless we have observed the distinct ferromagnetic intermolecular magnetic interaction. The present study provides the examples of the spin-transmission through diamagnetic compounds via inter-heteromolecular hydrogen bonding. In contrast to recent reports, which have demonstrated successful molecular and crystal designs by the use of inter-homomolecular hydrogen bond to realize a ferromagnetic interaction in the solid state,[9] our approach is the employment of the inter-heteromolecular hydrogen bond to constitute a supramolecular structure. We believe that boronic acid moieties are useful as ferromagnetic intermolecular spin coupler and building block of supramolecular structure.

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REFERENCES

1. A. Rajca, Chem. Rev., 94, 871 (1994); W. T. Borden, H. Iwamura and J. A. Berson, Acc. Chem. Res., 27, 109 (1994).
2. T. Akita, Y. Mazaki and K. Kobayashi, J. Chem. Soc., Chem. Commun., 1861 (1995); T. Akita, Y. Mazaki and K. Kobayashi, Mol. Cryst. Liq. Cryst., 279, 39 (1996).
3. B. Bettman, G. E. K. Branch and D. L. Yabroff, J. Am. Chem. Soc., 56, 1865 (1934).
4. E. F. Ullman, J. H. Osiecki, D. G. B. Boocock and R. Darcy, J. Am. Chem. Soc., 94, 7049 (1972).
5. W. Seaman and J. R. Johnson, J. Am. Chem. Soc., 53, 711 (1931).
6. G. H. Baker, Jr., G. S. Rushbrooke and H. E. Gilbert, Phys. Rev. A, 135, 1272 (1964); F. L. de Panthou, D. Luneau, J. Laugier and P. Ray, J. Am. Chem. Soc., 115, 9095 (1993)
7. H. M. McConnell, J. Chem. Phys., 39, 1910 (1963)
8. K. Awaga, A. Yamaguchi, T. Okuno, T. Inabe, T. Nakamura, M. Matsumoto and Y. Maruyama, J. Mater. Chem., 4, 1377 (1994)
9. E. Hernandez, M. Mas, E. Molins, C. Rovira and J. Veciana, Angew. Chem., Int. Ed. Engl., 32, 882 (1993); J. Cirujeda, L. E. Ochando, J. M. Amigo, C. Rovira, J. Rius and J. Veciana, Angew. Chem., Int. Ed. Engl., 34, 55 (1995); J. Cirujeda, M. Mas, E. Molins, F. L. de Panthou, J. Laugier, J. G. Park, C. Paulsen, P. Ray, C. Rovira and J. Veciana, J. Chem. Soc., Chem. Commun., 709 (1995); T. Sugawara, M. Matsushita, A. Izuoka, N. Wada, N. Takeda and M. Ishikawa, J. Chem. Soc., Chem. Commun., 1723 (1994)