Synthesis, Structure, and Magnetic Property of Manganese(II) Complex of 1,2-*closo*-Carboranyl Biradical with $S = 3/2$ Ground State

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Three-spin magnetic cluster consists of manganese(II) and *ortho*-carboranyl biradical **OCB-BNN** have been synthesized and characterized as the first example of the carborane containing paramagnetic complex. The crystal structure of discrete 1:1 complex $Mn(hfac)_2 \cdot$**OCB-BNN** was unambiguously determined. In the crystal structure, **OCB-BNN** behaves as the molecular tweezers that bind to manganese(II) ion. The strong antiferromagnetic interaction ($J/k_B = -181(2)$ K) was found between nitronyl nitroxides and manganese(II) ion.

There have been a number of reports on the syntheses and magnetic properties of the spin clusters containing organic radicals. The direct overlap between the magnetic orbitals of paramagnetic transition-metal ion and organic radical ensures significant magnetic exchange interaction. Because of the great advantage of the chelate effect that enforces the coordination of nitroxide, most organic radical ligands in spin-cluster complexes bear coordination subunits such as pyridine,[1] bipyridine,[2] ethylenediamine,[3] imidazole,[4] triazole,[5] phosphine oxides,[6] and so on. Recently, we have reported the synthesis and magnetic property of *ortho*-carboranyl biradical (**OCB-BNN**; Chart 1) having a weak through-space dipole intramolecular antiferromagnetic interaction.[7] Two nitroxide arms that held together by *ortho*-carborane cage might be suitable for the coordination to transition-metal ions with the aid of the chelate effect, therefore **OCB-BNN** should behave like molecular tweezers that can bind transition-metal ions, in spite of the absence of the assistance of the coordination sites.[8] The carborane framework is sometimes used for the construction of the supramolecular structures, however, the synthesis of carborane cluster compound having nonzero spin ground state is unexplored. The construction of magnetic carborane cluster is one of the productive approaches to the development of the boron material science. For the construction of the magnetic metal complex of **OCB-BNN**, we have chosen manganese(II) ion having $^6S_{5/2}$ ground state. The aim of our work in this communication is the synthesis, structural and magnetic investigation of the manganese(II) complex of *ortho*-carboranyl biradical as the first example of the transition-metal complex of the carborane derivative with nonzero spin ground-state.

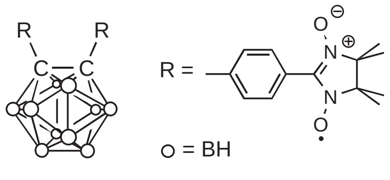

Chart 1.

In the usual way, 7.8 mg (15 µmol) of $Mn(hfac)_2 \cdot 2H_2O$ was azeotropically dehydrated in *n*-heptane. After the solution (ca. 5 mL) was cooled to room temperature, a solution of 9.6 mg of **OCB-BNN** (14 µmol) in 3 mL of dichloromethane was added and stirred 5 min. The color of the solution changed immediately from blue to green. The solution was concentrated to remove dichloromethane under reduced pressure then kept standing 20 min. The precipitation was filtered off and dried in vacuo to give 12.1 mg (11 µmol) of $Mn(hfac)_2 \cdot$**OCB-BNN** as green block crystals (yield; 79%). IR (KBr): $\nu_{B–H} = 2593\,\mathrm{cm}^{-1}$, $\nu_{N–O} = 1362\,\mathrm{cm}^{-1}$, $\nu_{C–F} = 1148–1254\,\mathrm{cm}^{-1}$.

The molecular structure revealed by X-ray crystallographic analysis is shown in Figure 1.[9] The long C1–C1^i [symmetry operator; (i) $-x + 1$, y, $-z + 1/2$] distance (1.718(6) Å) that result from the characteristic electronic state of carborane cage was found in the complex, however, there is no significant difference in the distance compared to that of free **OCB-BNN** (1.727(4) Å).[7] Manganese(II) ion is comprised of *trans*-coordination by nitroxides with 2.132(2) Å of bond lengths. The N–O distances are 1.272(3) Å (uncoordinated) and 1.302(3) Å (coordinated) and the N2–O2–Mn angle is 123.6(2)°. These bond lengths and angle are reasonable as compared with those found in manganese(II)-coordinated nitroxides in the literature.[10] The O2–Mn–O2^i and O3–Mn–O4^i angles are 157.1(1) and 157.40(8)°, respectively. The coordination environment of the manganese(II) is severely distorted from the octahedron. Although 3.542(4) Å of intermolecular contact in the adjacent uncoordinated NO···ON^{ii} was found [symmetry operator; (ii) $-x + 1/2$,

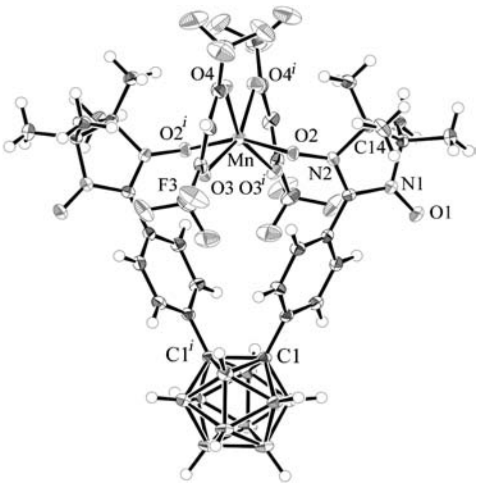

Figure 1. ORTEP view of $Mn(hfac)_2 \cdot$**OCB-BNN**. Hydrogen atoms are determined by calculation except those in carborane cage. The selected atom numbers are given in the figure.

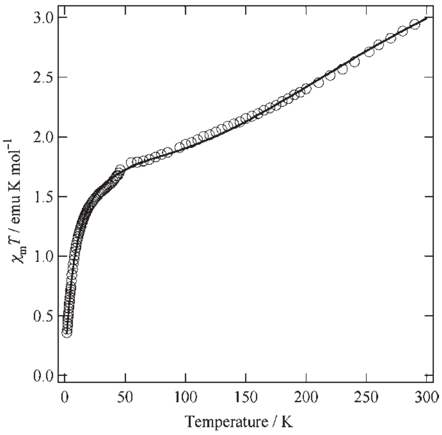

Figure 2. $\chi_m T$–T plot of Mn(hfac)$_2$•**OCB-BNN**. The solid curve is the theoretical fitting value that described in the text.

$-y+1/2$, $-z+1$], there is no effectual overlap between their magnetic orbitals in the molecular arrangement. Hence, a small contribution of the direct exchange is expected for the intermolecular magnetic interaction. On the other hand, a fluorine atom of hfac anion (F3) is held in close to O2^{iii} (3.241(3) Å), N2^{iii} (3.560(3) Å), and C14^{iii} (3.337(4) Å) of the other neighboring molecule [symmetry operator; (*iii*) $-x+3/2$, $-y+1/2$, $-z+1$]. Therefore, the intermolecular magnetic interaction through the superexchange path might play more important role for the magnetic behavior of Mn(hfac)$_2$•**OCB-BNN** rather than the direct exchange.

The temperature dependence of the product of magnetic susceptibility and temperature is shown in Figure 2. The magnetic interaction between manganese(II) and nitroxide radical is expected to be strongly antiferromagnetic due to the symmetry of the electronic ground state of the manganese(II).

At 300 K, $\chi_m T$ value is 3.0 emu K mol^{-1} much lower than the calculated uncorrelated spin-only value, 5.1 emu K mol^{-1}. This fact indicates that manganese(II) ion and nitroxide radicals are strongly coupled in antiferromagnetic manner in Mn(hfac)$_2$•**OCB-BNN**. The $\chi_m T$ value showed a gradual decrease as decreasing temperature, followed by the abrupt decrease attributable to the intermolecular interaction below 50 K to a value of 0.359 emu K mol^{-1} at 1.8 K. The magnetic interaction between the radicals through the carborane cage is probably very small in comparison with the direct exchange interaction between manganese(II) and radicals. Therefore, we carried out the analysis with linear three-spin model. On the basis of the Hamiltonian $\boldsymbol{H} = -J(\boldsymbol{S}_{\text{rad}} \cdot \boldsymbol{S}_{\text{Mn}} + \boldsymbol{S}_{\text{Mn}} \cdot \boldsymbol{S}_{\text{Rad}})$, the magnetic susceptibility data were analyzed by following equation (Eq 1), where J/k_B is intramolecular magnetic interaction between manganese(II) and radicals and the other symbols have their usual meaning.[11] The Lande factors were fixed to 2.0.

$$\chi' = \frac{N\mu_B^2 g^2}{4k_B T} \frac{35 + 35\exp(-J/k_B T) + 10\exp(-7J/2k_B T) + 84\exp(5J/2k_B T)}{3 + 3\exp(-J/k_B T) + 2\exp(-7J/2k_B T) + 4\exp(5J/2k_B T)}$$

$$\chi_m T = \frac{\chi' T}{1 - (2zJ'/Ng^2\mu_B^2)\chi'} \qquad (1)$$

A best-fit result is obtained as shown by the solid curve in Figure 2 with $J/k_B = -181(2)$ K. The large antiferromagnetic coupling constant is similar to other systems reported previously, and is consistent with the expectation based on the X-ray structure.[1–6,10,11a] A weak intermolecular antiferromagnetic interaction ($zJ'/k_B = -3.4(1)$ K) was taken into account by the mean-field approximation to reproduce the sudden decrease below 30 K.[12] The strong antiferromagnetic interactions between manganese(II) and nitroxides cause Mn(hfac)$_2$•**OCB-BNN** to be the magnetic cluster molecule with $S = 3/2$ ground state.

In conclusion, we have successfully synthesized three-spin magnetic system consists of manganese(II) and *ortho*-carboranyl biradical **OCB-BNN** as the first example of the carborane containing paramagnetic cluster. The construction of the spin-cluster molecule using **OCB-BNN** will contribute to the development of the boron material science and the supramolecular chemistry by means of carborane units.

This work was partly supported by a Grant-in-Aid for young scientists B (No. 16750125) from the MEXT, Japan. This work was also partially supported by a Grant-in-Aid for the 21st Century COE program (Aoyama Gakuin University) from the MEXT, Japan. F. I. and M. Y. thank the Japan Science and Technology Agency (JST) for financial support.

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9 Crystallographic data for Mn(hfac)$_2$•**OCB-BNN**: $C_{38}H_{44}N_4O_8B_{10}F_{12}Mn$, fw = 1075.81, monoclinic *C2/c* (#15), $a = 17.460(5)$ Å, $b = 20.740(5)$ Å, $c = 14.710(4)$ Å, $\beta = 110.160(4)°$, $V = 5000.4(2)$ Å^3, $Z = 4$, $T = 93(1)$ K. $R_1 = 0.059$, $R(R_w) = 0.074(0.131)$ (for all data), G.O.F. = 1.32 for 4322 unique reflections with $I > 2\sigma(I)$ and 345 variable parameters. Crystallographic data reported in this manuscript have been deposited with CCDC, No. CCDC-285276. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html.

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Published on the web (Advance View) December 10, 2005; DOI 10.1246/cl.2006.68