Synthesis, Structure, and Magnetic Property of Organic-radical Labeled Carborane

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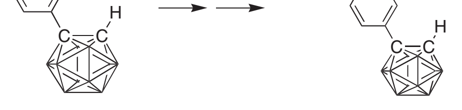
(Received August 17, 2004; CL-040972)

A carborane derivative containing nitronyl nitroxide group was synthesized and was crystallographically and magnetically characterized. The X-ray structure analysis revealed that the molecules were crystallized in a head-to-tail dimer fashion. The intradimer ferromagnetic interaction ($J/k_B = +4.26(2)$ K) was observed.

Extensive researches have been demonstrated on the chemistry of carboranes.[1] Taking advantage of the characteristic icosahedral framework, the carborane derivatives were often used for the modules for the molecular designing and crystal engineering.[2] The hydrogen-bonding affinity of the carborane derivatives due to their polarized C–H vertices has been applied for the crystal designing on the supramolecular chemistry.[3] On the one hand, constructions of organic magnetic materials are still attracting much attention. A nitronyl nitroxide is a prominent organic radical which has been played an essential part in the design and synthesis of organic magnetic materials. The bulk magnetism of the nitronyl nitroxide derivatives is drastically affected by the molecular alignment because intermolecular magnetic interactions play decisive role for their magnetic properties. In particular, an intermolecular hydrogen-bond is often important for the magnetic characters of the nitronyl nitroxide derivatives.[4]

The carborane derivatives can be considered as a novel spin-coupler. However, the preparation of organic radical substituted carboranes has not been mentioned up to date. In this paper, we would like to describe the synthesis, isolation and characterization of a carborane derivative containing a nitronyl nitroxide group.

Compound **1** (=2-[4′-[1″-(1″,2″-*o*-dicarba-*closo*-dodecacarboranyl)]phenyl]-4,4,5,5-tetramethylimidazolin-2-yl-1-oxyl-3-oxide) was synthesized from 4-[1″-(1″,2″-*o*-dicarba-*closo*-dodecacarboranyl)]benzaldehyde[5] and 2,3-dimethyl-2,3-bis(hydroxylamino)butane, followed by the oxidation using an aqueous sodium *meta*-periodide (Scheme 1).[6] The purification was performed by a column chromatography on silica gel using diethyl ether as an eluent. The eluent was kept standing for a few days and slowly evaporated. An X-ray-quality blue single crystal of **1** was obtained. The crystal structure of **1** is shown in Figure 1a.[7]



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Scheme 1. (i) 2,3-Dimethyl-2,3-bis(hydroxylamino)butane, MeOH, rt, 2 days. (ii) $NaIO_4$(aq), dichloromethane, 0 °C, 30 min.

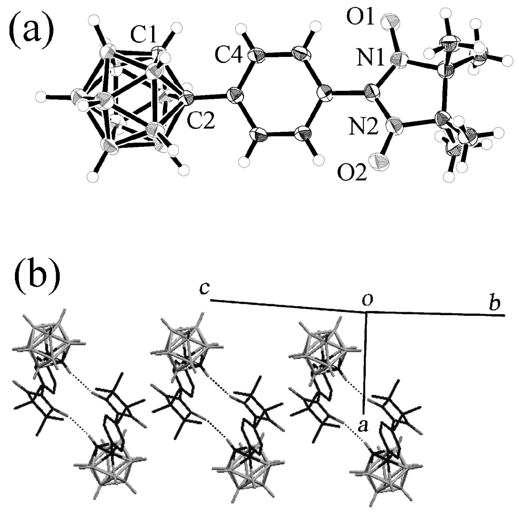

Figure 1. (a) An ORTEP drawing (50% of probability) of **1**. Hydrogen atoms of phenylene and methyl groups were determined by calculation. (b) A projection of the crystal packing of **1**. The broken lines represent the shortest contact described in the text.

The B–B bond lengths range from 1.763(7) to 1.796(7) Å. The C–C bond length in the icosahedron is 1.655(5) Å and the B–C bonds are in the range of 1.691(6) to 1.738(6) Å. Two N–O distances in the nitronyl nitroxide moiety are 1.286(4) and 1.291(4) Å. All of the bond lengths and angles found in **1** are reasonable as compared with those found in the literature. In the crystal lattice, the shortest intermolecular distance between O1 and $C1^i$ [symmetry operator; (i) $2-x$, $1-y$, $1-z$] was 3.160(5) Å. This intermolecular distance is comparable to those of the intermolecular hydrogen-bond lengths reported in the supramolecular structure of the carborane derivative.[3b] Therefore a significant intermolecular hydrogen-bonding will be expected. Because of this intermolecular hydrogen bond, two molecules of **1** are crystallized in a head-to-tail dimer manner as shown in

Figure 1b. The second nearest intermolecular distance lies between O1 and C4^i reproduced by the same symmetry operation. The dimer character observed in the magnetic measurement (see below) can be explained based on these structural features.

Magnetic property of isotropically oriented crystalline sample of **1** was measured by a SQUID magnetometer. Figure 2 shows the temperature dependences of the $\chi_m T$ product and the reciprocal magnetic susceptibility.

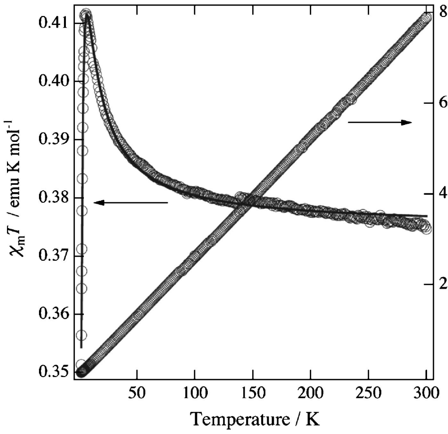

Figure 2. The temperature dependence of the magnetic property of **1**. The measurement was carried out under 0.5 T of the applied field.

The $\chi_m T$ value at room temperature (0.375 emu K mol^{-1}) corresponds to the theoretical value of the isolated $S = 1/2$ paramagnetic spin. On cooling, the $\chi_m T$ value gradually increased and reached a maximum (0.412 emu K mol^{-1}) at 5 K, followed by the steep decrease in the lower temperature region. This magnetic behavior clearly implies the presence of two different intermolecular magnetic interactions: firstly a ferromagnetic interaction that is predominant above ca. 5 K, secondly an antiferromagnetic one which dominates a bulk magnetism at cryogenic temperature.

Two options were used to analyze the magnetic behavior. (i) The reciprocal susceptibility of **1** was reproduced by means of the Curie–Weiss law ($\chi_m = C/(T - \theta)$) above 10 K. We obtained positive Weiss constant $\theta = +1.68(4)$ K indicating a small ferromagnetic intermolecular interaction. (ii) Taking into account the result of the X-ray crystal structure analysis, a singlet–triplet spin dimer model was used for the analysis. The modified Bleaney–Bowers equation (Eq 1) for the Hamiltonian $\boldsymbol{H} = -2J\boldsymbol{S}_1 \cdot \boldsymbol{S}_2$ was applied for the analysis of the magnetic data.[8] The parameter J is an intradimer magnetic interaction and zJ' describes a mean field intermolecular interaction.[9] The other symbols have their usual meanings. The best-fit parameters by the least-squares method in the overall temperature range were $J/k_B = +4.26(2)$ K and $zJ'/k_B = -0.61(1)$ K. The theoretical curve using these parameters is represented in Figure 2 by a solid line.

$$\chi_m = \frac{1}{\chi_{\mathrm{dimer}}^{-1} - 2zJ'/Ng^2\mu_B^2} \tag{1}$$

$$\chi_{\mathrm{dimer}} = \frac{Ng^2\mu_B^2}{k_B T}\,\frac{2}{3 + \exp(-2J/k_B T)}$$

The energy difference of two spin-states (singlet and triplet) for the experimental dimer structure of **1** (Figure 1b) was investigated by the single-point energy calculation at the UB3LYP/6-31G** level of theory. The calculation revealed that the triplet state is more stable in energy and is the ground state of the dimer. Moreover, the opposite spin densities in sign were found between O1 and H–(C1^i) and H–(C4^i). Therefore the ferromagnetic interaction is probably due to the spin polarization through these intermolecular short contacts described above.

In conclusion, we have successfully synthesized a new carborane derivative containing a nitronyl nitroxide as a spin source unit. Note that the ferromagnetic interaction was observed in this system. This is the first detection of the ferromagnetic intermolecular interaction in the hydrogen-bond network using a carborane cage. The isolation and characterization of **1** would help the development of the magnetic material science.

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.

References and Notes

1 a) J. F. Valliant, K. J. Guenther, A. S. King, P. Morel, P. Schaffer, O. O. Sogbein, and K. A. Stephenson, *Coord. Chem. Rev.*, **232**, 173 (2002). b) R. B. King, *Chem. Rev.*, **105**, 1119 (2001). c) V. I. Bregadze, *Chem. Rev.*, **92**, 209 (1992). d) J. Plesek, *Chem. Rev.*, **92**, 269 (1992). e) L. A. Leites, *Chem. Rev.*, **92**, 279 (1992).

2 A. Maderna, A. Herzog, C. B. Knobler, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **123**, 10423 (2001); W. Jiang, I. T. Chizhevski, M. D. Mortimer, W. Chen, C. B. Knobler, S. E. Johnson, F. A. Gomez, and M. F. Hawthorne, *Inorg. Chem.*, **35**, 5417 (1996).

3 a) R. J. Blanch, M. Williams, G. D. Fallon, M. G. Gardiner, R. Kaddour, and C. L. Raston, *Angew. Chem., Int. Ed. Engl.*, **36**, 504 (1997). b) M. G. Davidson, T. G. Hibbert, J. A. K. Howard, A. Mackinnon, and K. Wade, *Chem. Commun.*, **1996**, 2285.

4 a) K. Doi, T. Ishida, and T. Nogami, *Chem. Lett.*, **32**, 544 (2003). b) F. M. Romero, R. Ziessel, M. Bonnet, Y. Pontillon, E. Ressouche, J. Schweizer, B. Delley, A. Grand, and C. Paulsen, *J. Am. Chem. Soc.*, **122**, 1298 (2000). c) R. Endtner, E. Rentschler, D. Blaster, R. Boese, and R. Sustmann, *Eur. J. Org. Chem.*, **19**, 3347 (2000). d) T. Sugano, M. Kurmoo, H. Uekusa, Y. Ohashi, and P. Day, *J. Solid State Chem.*, **145**, 427 (1999). e) M. M. Matsushita, A. Izuoka, T. Sugawara, T. Kobayashi, N. Wada, N. Takeda, and M. Ishikawa, *J. Am. Chem. Soc.*, **119**, 4369 (1997).

5 M. G. H. Vicent, S. J. Shetty, A. Wickramasinghe, and K. M. Smith, *Tetrahedron Lett.*, **41**, 7623 (2000).

6 IR (KBr) $\nu_{\text{B-H}} = 2545$–$2619\,\mathrm{cm^{-1}}$, $\nu_{\text{N-O}} = 1365\,\mathrm{cm^{-1}}$; UV ($CH_2Cl_2$) $\lambda_{\max}$/nm (ε/M^{-1}cm^{-1}) = 275(15300), 282(15200), 294(15100), 374(14500). ESR (benzene solution, rt) showed characteristic five lines centered at $g = 2.006$ with hyperfine coupling constant $a_N = 0.73$ mT. Calcd For $C_{15}H_{27}N_2O_2B_{10}$: C, 47.98; H, 7.25; N, 7.46%. Found: C, 47.57; H, 7.11; N, 7.56%.

7 Crystallographic data for **1**: $C_{15}H_{27}N_2O_2B_{10}$, fw = 375.49, Monoclinic $P2_1/c$, $a = 7.363(4)$ Å, $b = 11.050(6)$ Å, $c = 25.74(1)$ Å, $\beta = 92.015(8)°$, $V = 2092.7(1)$ Å^3, $Z = 4$, $T = 120(1)$ K. $R(R_w) = 0.069(0.185)$, GOF = 0.84 for 6073 unique reflections with $I > 2\sigma(I)$ and 295 parameters. Crystallographic data reported in this manuscript have been deposited with CCDC as supplementary publication No. CCDC 247437. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html.

8 B. Bleaney and K. D. Bowers, *Proc. R. Soc. London, Ser. A*, **214**, 451 (1952).

9 C. J. O'Conner, *Prog. Inorg. Chem.*, **29**, 203 (1982).