Inorg. Chem. **2008**, *47*, 10217−10219

Inorganic Chemistry
Communication

Effects of Chemically Induced Contraction of a Coordination Polyhedron on the Dynamical Magnetism of Bis(phthalocyaninato)disprosium, a Single-4f-Ionic Single-Molecule Magnet with a Kramers Ground State

Naoto Ishikawa,*,† Yoshifumi Mizuno,† Satoshi Takamatsu,† Tadahiko Ishikawa,‡ and Shin-ya Koshihara‡

Department of Applied Chemistry, Chuo University, 1-13-27 Kasuga, Bunkyo-ku, Tokyo 112-8551, Japan, and Department of Materials Science, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152-8551, Japan

Received August 6, 2008

Chemically induced longitudinal contraction of the square-antiprism coordination polyhedron of a peripherically substituted bis(phthalocyaninato)dysprosiumate(III), a dysprosium-based single-4f-ionic single-molecule magnet having a $J_z = \pm^{13}/_2$ Kramers doublet ground state, resulted in drastic changes in dynamical magnetism including a doubling of the energy barrier, a 2-order-of-magnitude decrease of the spin reversal rate, a significant rise of the blocking temperature, and the first observation of the emergence of a large remanent magnetization.

The $(2J + 1)$-fold degeneracy of the ground state of a lanthanide ion in a complex, where J denotes the total angular momentum quantum number, is partly removed by the ligand field (LF). The substructure of the ground multiplet thus generated determines essential magnetic properties of the complex. It is therefore possible to "tune" the magnetic properties of a lanthanide complex by chemical or structural modification of the ligands through which the LF potential can be varied.

A certain type of LF can give a lanthanide ion an extremely large axial magnetic anisotropy associated with a slow transition rate between "spin-up" and "spin-down" states in such a degree that the ion behaves similarly to a classical magnet. Construction of a single-molecule magnet (SMM)[1−3] on this scheme was first achieved by employing double-decker phthalocyaninato (Pc) complexes with a trivalent terbium ion.[4] In the complex, the Tb^{3+} ion with a $4f^8$ electronic configuration is placed in a square-antiprism LF, which gives rise to a situation that $J_z = \pm 6$ sublevels are at the lowest energy in the $J = 6$ ground multiplet with an extremely large (about 400 cm^{-1}) energy gap from the rest of the sublevels.[5] This LF splitting pattern gives the complex long magnetic relaxation times (0.1 ms to 1 s) at a considerably high temperature range (up to 40 K).[4] It was recently pointed out that the phthalocyaninatolanthanide SMM is one of the most promising materials for use in molecular spintronic devices.[6]

Although the Pc−Tb complex showed slow magnetization relaxation at a considerably higher temperature range than any other known SMM systems, there was one drawback. The number of 4f electrons of Tb^{3+} is eight, which means that it is a non-Kramers system. In this case, the degeneracy of the doublet $J_z = \pm 6$ can be removed by an off-diagonal matrix element of the LF, which can become nonzero when the symmetry is lowered from the ideal D_{4d} point group.[7] The mixing of the two substates results in the loss of remanent magnetization at zero field.

A possible solution for this issue is to employ dysprosium ion Dy^{3+} having a $4f^9$ configuration, which is a Kramers system. The $J = {}^{15}/_2$ ground multiplet is split into eight doublets in the D_{4d} LF. The 2-fold degeneracy of any doublets including the lowest $J_z = \pm^{13}/_2$ pair is not removed by the LF. This means that the loss of remanent magnetization through mixing of the two states by the LF can be prevented.[7]

Previously, we reported that bis(phthalocyaninato)dysprosium anion $[Pc_2Dy^{III}]^-$ exhibited typical behavior as a SMM with temperature- and frequency-dependent alternating current (ac) magnetic susceptibility, although it was in a rather lower temperature range than that of the Tb complex.[4] The magnetization versus magnetic field ($M-H$) curve showed hysteresis

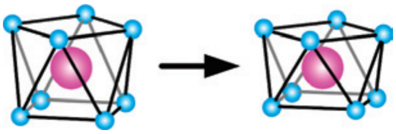
---

* E-mail: ishikawa@chem.chuo-u.ac.jp.
† Chuo University.
‡ Tokyo Institute of Technology.

(1) Christou, G.; Gatteschi, D.; Hendrickson, D. N.; Sessoli, R. *MRS Bull.* **2000**, *25*, 66.
(2) Sessoli, R.; Tsai, H.-L.; Schake, A. R.; Wang, S.; Vincent, J. B.; Folting, K.; Gatteschi, D.; Christou, G.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1993**, *115*, 1804.
(3) Sessoli, R.; Gatteschi, D.; Caneschi, A.; Novak, M. A. *Nature* **1993**, *365*, 141.
(4) (a) Ishikawa, N.; Sugita, M.; Ishikawa, T.; Koshihara, S.; Kaizu, Y. *J. Am. Chem. Soc.* **2003**, *125*, 8694. (b) Ishikawa, N.; Sugita, M.; Ishikawa, T.; Koshihara, S.; Kaizu, Y. *J. Phys. Chem. B* **2004**, *108*, 11265.
(5) (a) Ishikawa, N.; Sugita, M.; Okubo, T.; Tanaka, N.; Iino, T.; Kaizu, Y. *Inorg. Chem.* **2003**, *42*, 2440. (b) Ishikawa, N. *J. Phys. Chem. A* **2003**, *106*, 9543.
(6) Bogani, L.; Wernsdorfer, W. *Nat. Mater.* **2008**, *7*, 179.
(7) Ishikawa, N.; Sugita, M.; Wernsdorfer, W. *Angew. Chem., Int. Ed.* **2005**, *44*, 2931.

10.1021/ic8014892 CCC: $40.75

Scheme 1. Longitudinal Contraction of a Square-Antiprism Coordination Polyhedron



at 1.8 K but with a sharp drop at near zero field leaving practically no remanent magnetization because the relaxation time was not sufficiently long.[4]

The SMM behavior of these lanthanide complexes deeply depends on the energy gap between the lowest and second lowest sublevels in the ground multiplet, which approximately corresponds to the energy barrier for spin reversal. If one can increase the gap in some way, a slower spin reversal or a longer magnetization relaxation time would be obtained. In this Communication, we report that the two-electron oxidation of the Pc−Dy complex, which leads to a longitudinal contraction of the square-antiprism coordination polyhedron (Scheme 1), resulted in a significant increase of the effective barrier for spin reversal, a diminished spin reversal rate, and the emergence of a large remanent magnetization.

We have applied the previously reported method to reduce the height of the square-antiprism coordination polyhedron, in which the anionic bis(phthalocyaninato)lanthanide complex is oxidized by two electrons and the highest occupied molecular orbital, which is approximately an antibonding linear combination of the two highest occupied π orbitals of the two Pc ligands,[8] is vacated. This shortens the Pc−Pc distance and hence the height of the coordination polyhedron of the Dy ion.[9]

We used peripherically substituted Pc(OEt)$_8$, 2,3,9,10,16,17,23,24-octaethoxyphthalocyanine, instead of unsubstituted Pc for the ligand to overcome the extremely low solubility of the cationic complex $[\mathrm{Pc_2Dy^{III}}]^+$ to organic solvents. An electrically neutral complex $[\{\mathrm{Pc(OEt)_8}\}_2\mathrm{Dy}]^0$ was first prepared, and then anionic complex $[\{\mathrm{Pc(OEt)_8}\}_2\mathrm{Dy}]^-(n\text{-}\mathrm{Bu_4N})^+$ (**1**) was obtained by reducing the neutral complex with hydrazine monohydrate followed by the addition of $(n\text{-}\mathrm{Bu_4N})^+\mathrm{Br}^-$. The cationic complex $[\{\mathrm{Pc(OEt)_8}\}_2\mathrm{Dy}]^+(\mathrm{SbCl_6})^-$ (**2**) was obtained by oxidation with phenoxathiinylium hexachloroantimonate in dichloromethane. The end points of the redox reactions were determined using the characteristic spectra of the anionic and cationic Pc double-decker complexes in the UV region (Figure S1 in the Supporting Information).[10] Purification of **2** was carried out by recrystallization from a dichloromethane/hexane solution. Magnetic susceptibility measurements were carried out on a Quantum Design MPMS-XL SQUID magnetometer.

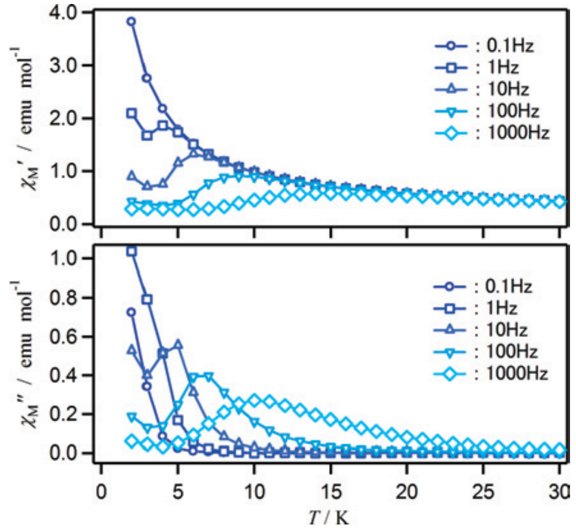


Figure 1. Plots of χ_M' (top) and χ_M'' (bottom) against temperature T, where χ_M' and χ_M'' are in-phase and out-of-phase ac molar magnetic susceptibilities, respectively, for a powder sample of the anionic complex **1** fixed in eicosane. The measurements were performed in a 5 G ac magnetic field oscillating at indicated frequencies with the absence of a direct current (dc) field.

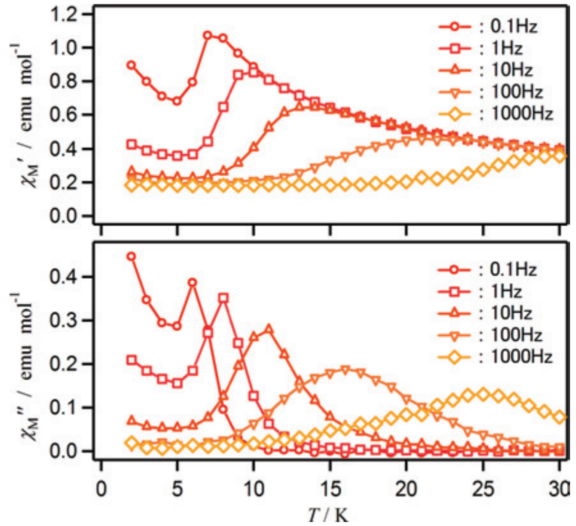


Figure 2. Plots of χ_M' (top) and χ_M'' (bottom) against temperature T for a powder sample of **2** fixed in eicosane. The measurements were performed in a 5 G ac magnetic field with the absence of a dc field.

Figure 1 shows the ac magnetic susceptibility of the anionic complex **1** as a function of the temperature measured with various ac-field frequencies. The Dy complex exhibits a sharp drop of χ' and peaks of χ'' at the temperature ranges dependent on the frequency, indicating that **1** is an SMM. The figure shows essentially the same temperature and frequency dependences as those of the unsubstituted compound $[\mathrm{Pc_2Dy}]^-\mathrm{TBA}^+$.[4] This indicates that the alkoxyl substituents on the Pc rings have little effect on the dynamical magnetism of the Dy complex as an SMM.

The effect of removing two electrons from Pc ligands is shown in Figure 2. The cationic complex **2** exhibited similar temperature and frequency dependences but in a significantly higher temperature range. The χ' drop and χ'' peak for an ac field of 10^3 Hz is observed at about 25 K, which is 15 K higher than that of **1** in the “normal” oxidation state.

The main relaxation path of magnetization of the Dy complexes in this temperature range is the Orbach process,[4] in which a transition between the two lowest sublevels occurs through absorption of a phonon to reach an excited state followed by emission of the second phonon.[11] The effective barrier height U_{eff}, which corresponds to the energy of the intermediate excited state, is estimated by Arrhenius analysis

---

(8) (a) Ishikawa, N.; Ohno, O.; Kaizu, Y.; Kobayashi, H. *J. Phys. Chem.* **1992**, *96*, 8832. (b) Ishikawa, N.; Ohno, O.; Kaizu, Y. *J. Phys. Chem.* **1993**, *97*, 1004.

(9) Takamatsu, S.; Ishikawa, N. *Polyhedron* **2007**, *26*, 1859–1862.

(10) Ishikawa, N. *J. Porphyrins Phthalocyanines* **2001**, *5*, 87.

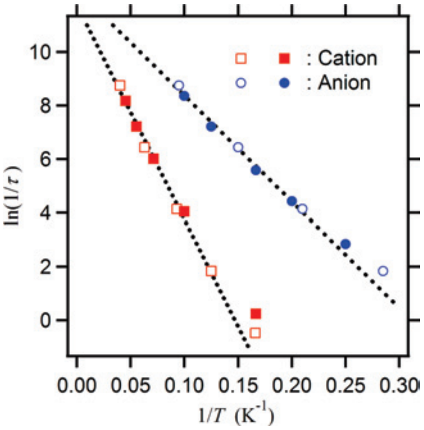


Figure 3. Plot of the natural logarithm of the inverse of the relaxation time τ against the inverse of the temperature T for **1** (circles) and **2** (squares). The open and closed marks represent the data obtained from χ'' vs T plots and those from χ'' vs f (frequency of the ac field) plots with fixed temperatures (4, 5, 6, 8, and 10 K for **1** and 6, 10, 14, 18, and 22 K for **2**), respectively. The broken lines represent the least-squares fit of the data from 5 to 10 K for **1** and from 10 to 25 K for **2** to the equation $\tau^{-1} = \tau_0^{-1} \exp(-U_{\mathrm{eff}}/kT)$.

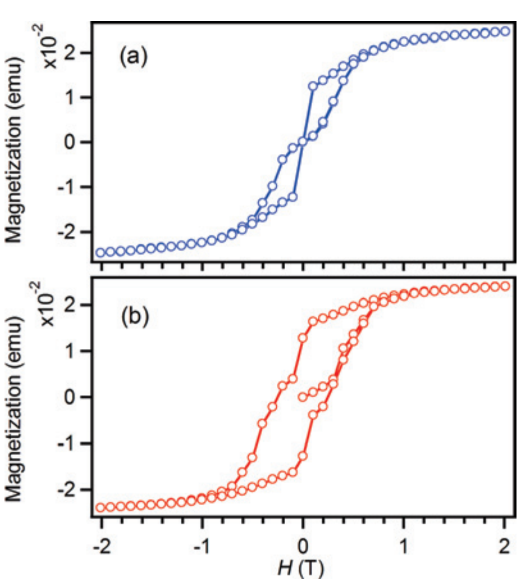


Figure 4. Magnetization vs dc magnetic field loop measured for powder samples of (a) **1** and (b) **2** at 1.8 K.

(Figure 3) to be 55 cm^{-1} for **2**, which is about twice as large as that of **1** (27 cm^{-1}).[12] Interestingly, in a similar experiment for the isostructural Tb complexes, the increase of the U_{eff} value was only 8%.[13]

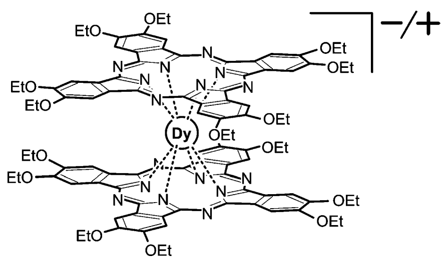
Figure 3 also shows that the cationic complex **2** has about a 2 orders of magnitude longer magnetization relaxation time τ than the anionic complex **1**. For example, at 10 K, the magnetization relaxation time τ of **1** is estimated at 2.3×10^{-4} s, whereas that of **2** is 1.8×10^{-2} s.

At this point, we have not reached a conclusion on the reason why the Dy complexes show a much larger increase in U_{eff} than Tb complexes, but one possible explanation is as follows. Using our previous model,[5] the energy gap between the $J_z = \pm 6$ doublet (lowest substates) and the $J_z = \pm 5$ doublet (second lowest) of the $[\mathrm{Pc_2Tb}]^{\pm}$ complex is written as

$$\Delta E(\mathrm{Tb}) = (1/3)A_2 + (\text{-}40/33)A_4 + (280/429)A_6 \qquad (1)$$

Here, A_k denotes the LF parameters $A_k^0\langle r^k\rangle$, whose values for unsubstituted $[(\mathrm{Pc})_2\mathrm{Ln}]^-$ have been reported in ref 5. The corresponding gap for the $[\mathrm{Pc_2Dy}]^{\pm}$ complex between $J_z = \pm{}^{13}/_2$ and $J_z = \pm{}^{11}/_2$ is

Scheme 2. Structure of $[\{\mathrm{Pc(OEt)_8}\}_2\mathrm{Dy}]^{\mp}$



$$\Delta E(\mathrm{Dy}) = (8/35)A_2 + (320/693)A_4 + (160/143)A_6 \qquad (2)$$

The important difference between the two cases is that the sign of the coefficient for A_4 is opposite to each other. This means that similar changes in the LF parameters can give significantly different changes in the energy gap.[14]

The two redox species showed clear hysteresis in the magnetization versus field ($M-H$) curves at 1.8 K, as seen in Figure 4. The most notable difference is that the cationic complex **2** exhibited a large remanent magnetization at zero field, whereas the anion **1** did not. Nonzero remanent magnetization of **2** was observed up to 4 K. This clearly shows that the relaxation time at zero field is increased significantly by the chemical modification of the LF at the Dy site.

In conclusion, we have shown that the dynamical magnetism of the single-Dy-ionic SMM is greatly altered by the modification of the LF potential, which is induced by a two-electron ligand oxidation. The large remanent magnetization expected for a Kramers system was observed. The effective barrier height U_{eff} of **2** was doubled from the original anionic form **1**. These findings contrast with our previous study for isostructural Tb complexes, in which the remanence remained very small and the increase of U_{eff} was more moderate.[13] Further investigation is in progress to clarify the mechanism of these observations by determining the multiplet substructures of the isostructural complexes with heavy lanthanide ions.

Acknowledgment. This work was partly supported by Chuo University, Inamori Foundation, and Tokuyama Science Foundation.

Supporting Information Available: UV−vis spectra of $[\{\mathrm{Pc(OEt)_8}\}_2\mathrm{Dy}]^-(n\text{-}\mathrm{Bu_4N})^+$, $[\{\mathrm{Pc(OEt)_8}\}_2\mathrm{Dy}]^+(\mathrm{SbCl_6})^-$, and $[\{\mathrm{Pc(OEt)_8}\}_2\mathrm{Dy}]^0$ in a chloroform solution. This material is available free of charge via the Internet at http://pubs.acs.org.

IC8014892

---

(11) Abragam, A.; Bleaney, B. *Electron Paramagnetic Resonance*; Clarendon Press: Oxford, U.K., 1970; Chapter 18.

(12) The preexponential factor in the Arrhenius equation $\tau^{-1} = \tau_0^{-1} \exp(-U_{\mathrm{eff}}/kT)$ was estimated at 1.2×10^5 s^{-1} for **2** and 2.2×10^5 s^{-1} for **1**. The increased τ_0 value also contributes to the elongation of τ of **2**.

(13) Takamatsu, S.; Ishikawa, T.; Koshihara, S.; Ishikawa, N. *Inorg. Chem.* **2007**, *46*, 7250.

(14) For example, using the LF parameters for $[\mathrm{Pc_2Tb}]^-\mathrm{TBA}^+$ in ref 5, if A_2 is increased by 20% while A_4 is decreased by 10%, the energy gap of the Tb case is changed from 436 to 449 cm^{-1} (+3%) and that of the Dy case is changed from 31.6 to 57.9 cm^{-1} (+83%).