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Cyclic Single-Molecule Magnet in Heterospin System

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Single-molecule magnets (SMMs)[1] showing slow magnetic relaxation are keenly anticipated as molecular nanomagnets and have been investigated intensively. One of the current interests for SMMs in the field of the molecule-based magnet is the formation of SMMs with a high activation barrier, U_{eff}, for the reorientation of the magnetism.[2] Based on the idea of the heterospin system[3] consisting of a 3d spin for the anisotropic metal ion and a 2p spin for the organic spin, we prepared heterospin monocobalt complexes carrying organic spins such as aminoxyls and carbenes. The obtained heterospin cobalt complexes exhibited SMM magnetic behavior with large U_{eff} values of 89−20 K in diluted frozen solutions[4] and in the crystalline state.[5] As shown in these cobalt complexes, this heterospin systems can be used to prepare various SMMs by varying the combination of the high-spin cobalt(II) complex and the organic spins. We further demonstrated the formation of SMMs with the quartet ground state ($S_{total} = ^3/_2$), which is the smallest value among the SMMs reported to date, by using bi- and tridentate cobalt complexes and organic spins.[6] To obtain an SMM having a high U_{eff} value in the heterospin system, this time, the photoresponsive magnetic coupler[7] connecting two pyridine ligands by carbene was employed. Didiazo-dipyridine ligand **D2py$_2$(TBA)**, which is a precursor of the corresponding carbene derivative and is known to produce a high-spin carbene with quintet ground state ($S = ^4/_2$) after irradiation,[8] was used as a bridging ligand between the cobalt complex units. In this study, we report the crystal structure of the dinuclear cobalt(II) complex composed of **D2py$_2$(TBA)** and **Co(hfpip)$_2$**; bis{1,1,1,5,5,5-hexafluoro-4-(4-*tert*-butylphenylimino)-2-pentanonate}cobalt and its magnetic behavior after irradiation in a crystalline state.
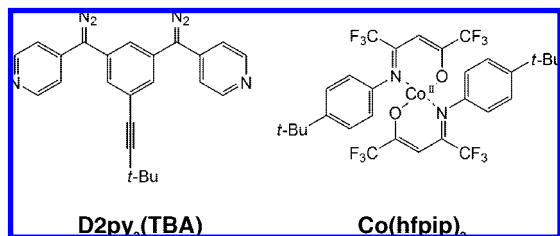
D2py$_2$(TBA)   **Co(hfpip)$_2$**

Didiazo-dipyridine ligand **D2py$_2$(TBA)** and the cobalt complex **Co(hfpip)$_2$**, chelating with bidentate ligand, hfpip, were prepared by the modified procedure reported previously.[9] The 2:2 cobalt(II) complex [**Co(hfpip)$_2$(D2py$_2$(TBA))**)]$_2$, **1**, was obtained as single crystals of the dark red bricks from the solution of the mixtures of **Co(hfpip)$_2$** in *n*-hexane and **D2py$_2$(TBA)** in CH$_2$Cl$_2$ at 4 °C. The molecular structure of **1** revealed by X-ray crystallography (Table S1) has one symmetry centered in a molecule, and the cobalt ion units have compressed octahedral structures in which two **D2py$_2$(TBA)** are coordinated in a *cis* configuration (Figure 1). The bond lengths between the cobalt ion and the axial ligands (Co−O1 and O2) are shorter by 0.14−0.20 Å than the others. The dihedral
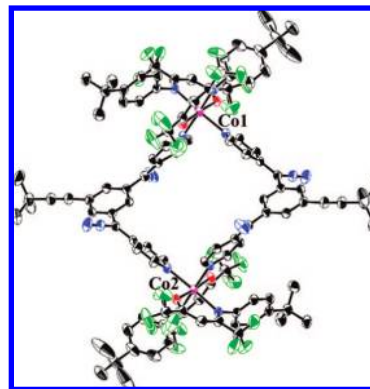
Figure 1. ORTEP drawing of the molecular structure of [**Co(hfpip)$_2$(D2py$_2$(TBA))**)]$_2$, **1**. Hydrogen atoms and molecules of CH$_2$Cl$_2$ and *n*-hexane were omitted for the sake of clarity. Color code: Co, purple; N, blue; F, green; O, red.

angles between the pyridine plane and the $X−Y$ plane defined by four atoms coordinating to the cobalt ion are 62.55° and 80.26°. The distance between the cobalt ions in a molecule is 11.3 Å, indicating that the direct Co1−Co2 interaction might be insignificant. In the crystal packing (Figure S1), no short distances (<4 Å) resulting in intermolecular magnetic coupling were observed, suggesting that the complex might be magnetically isolated in the crystalline state.

It is noted that photolysis of diazo groups in this complex effectively took place in a crystalline state. Therefore, the microcrystal of **1** (ca. 0.5 mg), which was spread on the sellotape, could be used as a sample for SQUID measurement.

In this study, the dc and ac magnetic susceptibility data of the microcrystalline sample of **1** were collected under three conditions, before and after irradiation and then after annealing at 70 K which is a temperature lower than that at which the carbene units start to decompose chemically. Before irradiation, the $\chi_{mol}T$ values in a $\chi_{mol}T$ vs T plot were nearly constant (3.8 cm^3·K·mol^{-1}) in the temperature range 1.9−20 K. On photolysis, the M value steeply increased and reached the saturation value after irradiation for 55 h (Figure S2). The yield of photolysis of the sample was determined to be ca. 85% by the disappearance of the IR absorption at 2058 cm^{-1} due to the diazo moieties in the complex after SQUID measurements.

In the $\chi_{mol}T$ vs T plot after irradiation, the $\chi_{mol}T$ values were nearly constant (26 cm^3·K·mol^{-1}) for 15−30 K and gradually decreased below 15 K (Figure S3). After annealing at 70 K, complex **1** showed a similar $\chi_{mol}T$ vs T plot with a constant value of 25 cm^3·K·mol^{-1}. These constant values are much larger than that (9.8 cm^3·K·mol^{-1}) calculated by a spin-only equation with two isolated quintet carbenes (3.0 cm^3·K·mol^{-1} × 2) and two high-spin cobalt(II) ions with effective spin $S' = ^1/_2$ ($\chi_{mol}T$ value of 3.8 cm^3·K·mol^{-1} before irradiation), suggesting that the carbenes and
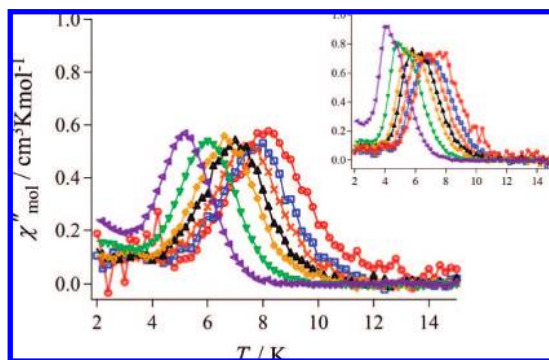
Figure 2. Plots of χ''_{mol} vs T with a 5 Oe ac field oscillating at 1000 (red), 500 (blue), 250 (orange), 100 (black), 50 (yellow), 10 (green), and 1 (purple) Hz obtained after irradiation of the microcrystalline sample of **1** before (inset) and after annealing at 70 K.
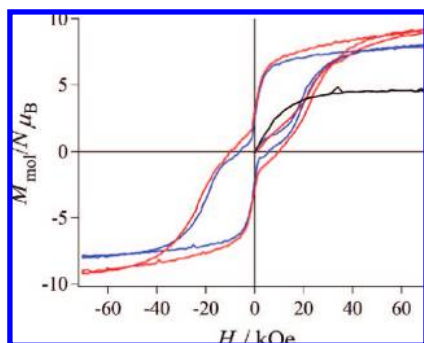

Figure 3. Hysteresis loop of **1** (black) before and (blue) after irradiation and then (red) after annealing at 70 K.

the cobalt ions in the complex interacted ferromagnetically to form the high-spin ground state with $S_{total} = {}^{10}/_2$ and $g = 2.63$. The decrease in the $\chi_{mol}T$ values below 15 K indicate an effect of the zero-field splitting caused by spin−orbit coupling in the cobalt ion.

Ac magnetic susceptibility measurements at a zero dc field with a 5.0 Oe ac field were carried out in the temperature range 1.9−15 K. Before irradiation, no χ''_{mol} signals (out-of-phase signal) were observed, while, after irradiation, well-resolved χ'_{mol} (in-phase signal) and χ''_{mol} signals with a frequency dependence were observed (Figures S4 and 2). As observed in Figure 2, χ''_{mol} signals at each frequency showed a maximum above 1.9 K and the peak-top temperature shifted lower as the frequency decreased. These observations after irradiation indicate that the cobalt−carbene complex has a slow magnetic relaxation for reorientation of the magnetism. Furthermore, the peak-top temperature at each frequency before annealing shifted higher with a slightly weak intensity after annealing. The activation energy, U_{eff}, for flipping the spin and the pre-exponential factor, τ_0, were estimated from the Arrhenius plot: $\tau = 1/2\pi\nu = \tau_0 \exp(U_{eff}/k_B T)$ to give $U_{eff} = 69$ K and $\tau_0 = 1.2 \times 10^{-8}$ s before annealing and 96 K and 1.4×10^{-9} s after annealing.

The field dependence of dc magnetization, M_{mol}, was measured in the range −70 to +70 kOe with a field-sweeping rate of 0.35 kOe/s below 5 K. In the $M_{mol}/N\mu_B$ vs H plots before and after annealing (Figure 3), the hysteresis loops relating to the field were observed below ca. 5 K (Figure S5) and showed abrupt changes of $M_{mol}/N\mu_B$ value at 0 kOe due to the spin quantum tunneling. The width of the hysteresis loops depends on the temperature and increased with decreasing temperature. The coercive force, H_c, and the remnant magnetization, M_r, at 1.9 K are ca. 6 kOe and 1.4 × 10^4 cm³·Oe·mol⁻¹ before annealing and 10 kOe and 1.7 × 10^4 cm³·Oe·mol⁻¹ after annealing, respectively.

The difference of magnetic behavior observed before and after annealing might be due to the change of local environments around the cobalt ion and the carbene centers caused by the release of nitrogen gas. A similar change of U_{eff} value was also observed in the 1:4 complex of the cobalt with pyridine-aminoxyls, which had a U_{eff} value of 28 K in the crystalline state and 48 K in the frozen solution.[5]

After annealing at the temperature above 200 K, the magnetic behavior observed after irradiation disappeared and returned to that before irradiation. This result clearly indicates that the magnetic interactions between the anisotropic cobalt ion and the carbenes generated by photolysis produce the observed SMM character. In summary, a cyclic 2:2 complex, **1**, of the cobalt complex, **Co(hfpip)₂**, and photoresponsive magnetic coupler, **D2py₂(TBA)**, was prepared, which was photolyzable in the crystalline state. After irradiation of the crystal of **1**, a strong frequency dependence of χ'_{mol} and χ''_{mol} signals, a physically reasonable value of τ_0, and a temperature-dependent hysteresis loop were observed, indicating that the SMM was formed. Co−carbene complex **1** was an SMM with $U_{eff} = 69$ K and $H_c = 6$ kOe at 1.9 K and then changed to the one with $U_{eff} = 96$ K, which is the largest value so far, and $H_c = 10$ kOe at 1.9 K after annealing at 70 K.

Attempts to create a single-chain magnet[1] by using a combination of **Co(hfpip)₂** and a photoresponsive magnetic coupler in the heterospin system are in progress.

Supporting Information Available: Crystallographic details (CCDC No. 684692, CIF), crystal data (Table S1), M vs $time$ plot (Figure S2), the $\chi_{mol}T$ vs T plot (Figure S3), $\chi'_{mol}T$ vs T plot (Figure S4), and temperature dependence of hysteresis loop of **1** (Figure S5). These materials are available free of charge via the Internet at http://pubs.acs.org.

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