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Heterospin Single-molecule Magnets with Extra-large Anisotropic Barrier

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ABSTRACT
The mixtures of Co(X-hfpip)$_2$; X = I and H, and bisdiazodipyridine ligands, D$_2$py$_2$(TBA), in 1:1 ratios gave the discrete cobalt complexes, 1 and 2, respectively. The molecular structures for 1 and 2 revealed by X-ray crystallography were cyclic 2:2 cobalt complexes formulated as [(Co(X-hfpip)$_2$)$_2$(D$_2$py$_2$(TBA))$_2$], in which the cobalt units were compressed octahedra. After irradiation of the microcrystalline samples, the resulting Co-carbene complexes, 1c and 2c, showed SMM behaviors exhibiting slow magnetic relaxations. In dc and ac magnetic susceptibility experiments, the activation barrier, $U_{\text{eff}}$, for reorientation of the magnetic moment were estimated to be 139 and 135 K for 1c and 2c, respectively, and the hysteresis loops of the magnetization (the coercive force, $H_c$, and 26 and 15 kOe at 1.9 K for 1c and 2c, respectively) were observed. In addition, the values of the quantum tunneling time, $\tau_Q$, were determined to be $1.1 \times 10^5$
and $5.4 \times 10^5$ sec ($t_{1/2} = 21$ and 104 hours) for 1c and 2c, respectively, below 2.5 K.

Keywords: heterospin system, single-molecule magnet, cobalt(II) complex, carbene, hysteresis loop.

1. Introduction

A topic of current interest regarding single-molecule magnets (SMM) [1] in the field of the molecule-based magnet is the construction of SMM with a high effective activation barrier, $U_{\text{eff}}$, for reorientation of the magnetic moment.[2] An SMM with a large $U_{\text{eff}}$ value leading to a high blocking temperature, $T_B$, below which the molecule becomes a magnet, is anticipated as a next-generation functional material, a nm-size magnet. In SMM, the characteristic slow magnetic relaxation for reorientation of the magnetic moment takes place via two pathways due to the thermal activation barrier $U$ corresponding to $|D|S^2$, where $|D|$ ($D < 0$) is a uniaxial anisotropic parameter and $S$ is a spin quantum number, and the quantum tunneling of the magnetization (QTM) [3] relating to the transverse anisotropic parameter, $E$. To obtain a large value of $U_{\text{eff}}$ ($U > U_{\text{eff}}$), therefore, an increasing $U$ value and/or a suppressing QTM pathway are required. Based on the strategy of the heterospin system [4] consisting of organic spins and metal ions, we have prepared heterospin SMMs [5] with relatively large $U_{\text{eff}}$ values. Recently, a cyclic 2:2 complex, $[(\text{Co(tert-Bu-hfpip)}_2)_2(\text{D}_2\text{py}_2(\text{TBA}))_2]$, composed of the cobalt complex, $\text{Co(tert-Bu-hfpip)}_2$; bis{1, 1, 1, 5, 5, 5, hexafluoro-4-(4-tert-butyphenylimino)-2-pentanonate} cobalt and photoresponsive magnetic coupler, $\text{D}_2\text{py}_2(\text{TBA})$, was found to be photolyzable in the crystalline state and exhibited an SMM behavior with $U_{\text{eff}} = 96$ K and $H_c = 10$ kOe at 1.9 K after irradiation and then annealing at 70 K. [6] To alterate the local circumstance of cobalt ions in this heterospin system, this time, diazo-substituted Co(hfpip)$_2$ complexes, $[(\text{Co(X-hfpip)}_2)_2(\text{D}_2\text{py}_2(\text{TBA}))_2]$; $X = \text{H, I, Br, NO}_2$ and $\text{CF}_3$, were prepared and the substituent effects of the hfpip cobalt complexes on the SMM magnetic properties were investigated. In these complexes, we found the iodo and no substituent complexes, $[(\text{Co(I-hfpip)}_2)_2(\text{D}_2\text{py}_2(\text{TBA}))_2]$, 1, and $[(\text{Co(hfpip)}_2)_2(\text{D}_2\text{py}_2(\text{TBA}))_2]$, 2, exhibiting SMM behaviors with extra-large anisotropic barriers after irradiation. Interestingly, in these complexes, the temperature-independent magnetization decays due to QTM were
observed in 2.5 – 1.9 K. In this paper, we reported the molecular structures of 1 and 2, their SMM behaviors after irradiation, and the comparison of the SMM properties with that for [(Co(tert-Bu-hfpip)2(D2py2(TBA))2], 3, reported previously [6].

2. Experimental

2.1. General

Infrared spectra were recorded on a JASCO 420 FT-IR spectrometer. Melting points were obtained with a MEL-TEMP heating block and are uncorrected. Elemental analyses were performed in the Analytical Center of the Faculty of Science in Kyushu University.

2.2. X-ray Crystal and Molecular Structure Analyses

Crystallographic data and experimental details for D2py2(TBA), 1, and 2, are summarized in Table 1. Suitable single crystals were glued onto a glass fiber using epoxy resin. All X-ray data were collected on a Rigaku Raxis-Rapid diffractometer with graphite monochromated MoKα radiation (λ = 0.71069 Å). Reflections were collected at 123 ± 1 K. The molecular structures were solved by direct methods (SIR program) and expanded using Fourier techniques (DIRDIF94). The refinements were converged using the full-matrix least squares method from the Crystal Structure software package [7] to give the P-1 (no. 2) for D2py2(TBA), 1, and 2. All non-hydrogen atoms were refined anisotropically, hydrogen atoms were included at standard positions (C-H = 0.96
Å, C-C-H = 120 °) and refined isotropically using a rigid model. Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-803425, 734081, and -803858 for D2py2(TBA), 1, and 2, respectively.

Table 1
Crystallographic data of D2py2(TBA), 1, and 2

<table>
<thead>
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<th>D2py2(TBA)</th>
<th>1</th>
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<tr>
<td>empirical formula</td>
<td>C24H20N6</td>
<td>C92H60F24N16O4I4Co2</td>
<td>C92H64N16O4F24Co2</td>
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<tr>
<td>$D_{calc}$ (g/cm$^3$)</td>
<td>1.274</td>
<td>1.699</td>
<td>1.501</td>
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<td>Color</td>
<td>Red</td>
<td>Red</td>
<td>Red</td>
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<tr>
<td>radiation</td>
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<td>Mo-K$_\alpha$</td>
<td>Mo-K$_\alpha$</td>
</tr>
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<td>$R_p$, $wR_2$ [$I &gt; 2\sigma(I)$]</td>
<td>0.062, 0.196</td>
<td>0.068, 0.212</td>
<td>0.067, 0.192</td>
</tr>
<tr>
<td>GOF</td>
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<td>1.120</td>
<td>1.052</td>
</tr>
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<td>29271</td>
<td>9214</td>
</tr>
<tr>
<td>No of variables</td>
<td>272</td>
<td>722</td>
<td>740</td>
</tr>
</tbody>
</table>

$R_1 = \Sigma \left| F_0 \right| - \left| F_c \right|/ \Sigma \left| F_0 \right|; wR_2 = \left\{ \sum w(F_0^2 - F_c^2)^2/ \sum w(F_0^2)^2 \right\}^{1/2}$

2.3. Measurements and Analyses of Magnetic Properties

Direct current (dc) and alternating current (ac) magnetic susceptibility data were obtained on a Quantum Design MPMS5S SQUID magneto/susceptometer, and corrected for the magnetization of the sample holder and capsule, and for diamagnetic
contributions to the samples, which were estimated from Pascal’s constants [8]. The concentrations of the starting diazo-cobalt complexes were used as those of the samples after irradiation. Ac magnetic susceptibility measurements were carried out with a 3.9 Oe oscillating field and a zero dc field at a frequency of 1 - 997 Hz. Photolyses of the samples were performed inside a sample room of SQUID by using the irradiation system reported previously [4].

2.4. Materials

Bisdiazo-dipridyl ligand, D2py2(TBA), and the cobalt complexes, Co(X-hfip)2; X = I and H, were prepared by the procedure reported previously. [6, 9]

D2py2(TBA); Solutions of D2py2(TBA) in CH2Cl2 and CH3CN were kept at 4 °C to afford the single crystals as of red bricks. m.p. (dec.) 126 °C, IR (KBr disck.) 2049 cm⁻¹, Anal. Calcd for C24H20N6 : C 73.45, H 5.14, N 21.41; found: C 73.16, H 5.10, N 21.34.

[(Co(I-hfip)2)2(D2py2(TBA))2], 1; Solutions of diazo-dipridine ligand D2py2(TBA)2 (32 mg, 0.08 mmol) in CH2Cl2 (4 mL) and cobalt complex Co(I-hfip)2 (70 mg, 0.08 mmol) in CH3CN (4 mL) were mixed and kept at 4 °C. The 2:2 cobalt(II) complex, 1, was obtained as single crystals of dark red bricks. m.p. (dec.) 153 °C, IR (KBr disck.) 2058 cm⁻¹, Anal. Calcd for C92H60F24N16O4Co2/0.5CH2Cl2: C 43.59, H 2.39, N 8.84; found: C 43.52, H 2.44, N 8.82.

[(Co(hfip)2)2(D2py2(TBA))2], 2; Solutions of diazo-dipridine ligand D2py2(TBA) (30 mg, 0.08 mmol) in CH2Cl2 (4 mL) and cobalt complex Co(hfip)2 (48 mg, 0.08 mmol) in n-hexane (4 mL) were mixed and kept at 4 °C. The 2:2 cobalt(II) complex, 2, was obtained as single crystals of dark red bricks. m.p. (dec.) 142 °C, IR (KBr disck.) 2058 cm⁻¹, Anal. Calcd for C92H64F24N16O4Co2/0.5CH2Cl2: C 54.39, H 3.18, N 11.03; found: C 54.51, H 3.17, N 11.03.

3. Results and Discussion

3.1. X-ray Molecular Structure Analysis of D2py2(TBA), [Co(I-hfip)2(D2py2(TBA)) 2], 1, and [Co(hfip)2(D2py2(TBA)) 2], 2
The single crystals of D$_2$py$_2$(TBA), [Co(I-hf pip)$_2$(D$_2$py$_2$(TBA))$_2$], 1, and [Co(hf pip)$_2$(D$_2$py$_2$(TBA))$_2$], 2 were analyzed by X-ray crystallography.

(A) D$_2$py$_2$(TBA)
ORTEP drawing of the molecular structure is shown in Fig. S1. Two diazo moieties in a molecule direct opposite direction and the dihedral angles between the benzene plane and the pyridine plane are 49.0 and 63.5°, respectively.

(B) [Co(I-hf pip)$_2$(D$_2$py$_2$(TBA))$_2$], 1, and [Co(hf pip)$_2$(D$_2$py$_2$(TBA))$_2$], 2
The single crystals contained four CH$_2$Cl$_2$ and two CH$_3$CN molecules for 1 and four CH$_2$Cl$_2$ molecules for 2 used for the recrystallization. Complexes, 1 and 2, were crystallized in the P-1 space group and both complexes and 3 were isomorphous with similar bond lengths and angles. The molecules of 1 and 2 had one symmetry center at the center of the cyclic molecule and the latter showed the disorders at C(20)-tert-butyl groups and diazo (N2-N3) moieties. In the molecular structure, two D$_2$py$_2$(TBA)s bridged two Co(X-hf pip)$_2$ by cis coordination to form a cyclic dinuclear complex. ORTEP drawings of molecular structure for 1 and 2 are shown in Fig. 1.
The local structure of the cobalt ion unit is a compressed octahedron in which the bond lengths between the cobalt ion and the axial ligands (Co–O1 and O2) are shorter by 0.13 - 0.18 Å and 0.15 - 0.18 Å for 1 and 2, respectively, than the others. The dihedral angles between the pyridine plane and the X-Y plane defined by four atoms coordinating to the cobalt ion are 73.22 and 81.16° for 1 and 75.18 and 80.11° for 2. In bridging ligand, D2py2(TBA), diazo moieties direct opposite direction and the dihedral angles between the pyridine ring and the phenyl ring are 56.4 and 62.1 ° for 1 and 53.4 and 56.9 ° for 2. These angles were consistent with those (49.0 and 63.5 °, Fig. S1) for free D2py2(TBA), indicating that 1 and 2 have no strain caused by the complexation with Co(X-hfpipe)2. The intramolecular Co–Co distances are 12.37 Å and 11.90 Å for 1 and 2, respectively. No significant intermolecular short contacts were observed within 6 Å in the crystal packing (Fig. S2). Selected bond lengths and dihedral angles for 1 and 2 together with those for 3 are summarized in Table 2. Noticable difference of the molecular structures in three complexes, 1, 2, and 3, was observed in the dihedral angle between the pyridine plane and the X-Y plane. In 3, the those angles are 80.26 and 62.55 ° and the second value is small compared with the first one and those for the correspinding angles in 1 and 2. The observed small dihedral angle might reduce the magnetic interaction between the cobalt ion and the carbene generated by photolysis.
Table 2.
Selected Bond Lengths (Å) and Dihedral Angles (°) for 1, 2, and 3

<table>
<thead>
<tr>
<th></th>
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<td>Co-N(1)</td>
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<td>Co-N(6)</td>
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<td>Co-O(2)</td>
<td>2.030</td>
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<tr>
<td>Co-Co</td>
<td>12.37</td>
<td>11.90</td>
<td>11.31</td>
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<td>Dihedral Angles (°) between Pyridine Ring and XY Plane</td>
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<tr>
<td>N(1)N(6)N(7)N(8)</td>
<td>73.22</td>
<td>80.11</td>
<td>80.26</td>
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<tr>
<td>-N(1)C(2)C(4)</td>
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<tr>
<td>N(1)N(6)N(7)N(8)</td>
<td>81.16</td>
<td>75.18</td>
<td>62.55</td>
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<td>-N(6)C(15)C(18)</td>
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<td>N(1)C(2)C(4)</td>
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<td>56.92</td>
<td>54.55</td>
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<tr>
<td>-C(8)C(10)C(12)</td>
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<tr>
<td>N(6)C(15)C(18)</td>
<td>62.12</td>
<td>53.40</td>
<td>55.88</td>
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<td>-C(8)C(10)C(12)</td>
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</table>

^a ref [6]

3.2. Magnetic properties

3.2.1. Photolyses of microcrystalline samples of 1 and 2

Crystalline 1 and 2 (ca. 0.5 mg) ground and spread on cellophane tape were used as samples. Photolyses of the samples were performed in the sample room of SQUID apparatus through an optical fiber using light from an argon ion laser at \( \lambda = 514 \text{ nm} \) below 10 K. The progress of photolysis was followed by \( M \) measurement at the constant field of 5 kOe and at 5 K. On photolysis, the \( M \) value for photoproducts, 1c and 2c, steeply increased and reached a saturation value after irradiation for 20 - 36 hrs. The
plot of $M$ vs. time for 1 is shown in Fig. 2. The yields of photolysis of 1 and 2 were determined to be ca. 85 and 82 %, respectively, from the disappearance of the IR absorption at 2058 cm$^{-1}$ due to the diazo moieties in the complex after SQUID measurements.

Fig. 2. Plot of $M$ vs. irradiation time for 1 at ca. 5 K

3.2.2. Dc magnetic susceptibility measurements

The values of dc molar magnetic susceptibility, $\chi_{\text{mol}}$, before and after irradiation of 1 and 2 were collected at the constant field of 5 kOe below 30 K. Obtained $\chi_{\text{mol}}$ values were plotted in a fashion of $\chi_{\text{mol}}T$ vs. $T$ plot, as shown in Fig. 3. Before irradiation, the $\chi_{\text{mol}}T$ values in the $\chi_{\text{mol}}T$ vs. $T$ plot were nearly constant (4.0 cm$^3$Kmol$^{-1}$) in the temperature range of 1.9–10 K. After irradiation, the $\chi_{\text{mol}}T$ values for 1e were nearly constant (29 cm$^3$Kmol$^{-1}$) for 15 – 30 K and gradually decreased below 8 K (Fig. 3). Complex 2e also showed a similar thermal profile of $\chi_{\text{mol}}T$ in $\chi_{\text{mol}}T$ vs. $T$ plot and a constant $\chi_{\text{mol}}T$ value of 24 cm$^3$Kmol$^{-1}$ was obtained (Fig. S3). These constant values are much larger than that (10.0 cm$^3$Kmol$^{-1}$) calculated by a spin-only equation with two isolated quintet carbenes (3.0 cm$^3$Kmol$^{-1}$ x 2) and two high-spin cobalt(II) ions with effective spin $S_{\text{eff}} = 1/2$ ($\chi_{\text{mol}}T$ value of 4.0 cm$^3$Kmol$^{-1}$ before irradiation) [8, 10], suggesting that the carbenes and the cobalt ions in the complex interacted ferromagnetically to form a high-spin ground state with $S_{\text{total}} = 10/2$. The decrease in the
\( \chi_{\text{mol}} T \) values for both complexes below 8 K indicates an effect of the zero-field splitting caused by spin-orbit coupling in the cobalt ion.

Fig. 3. Plots of \( \chi_{\text{mol}} T \) vs. \( T \) before (filled) and after irradiation (open) of 1.

The field dependencies of dc magnetization, \( M_{\text{mol}} \), for 1c and 2c were measured in the range -50 to +50 kOe with a field-sweep rate of 0.35 kOe/sec at the various temperatures below 6 K. The \( M_{\text{mol}} \) vs. \( H \) plots at various temperatures below 6 K for 1c and 2c are shown in Fig. 4.
**Fig. 4.** Hysteresis loops of 1c (a) and 2c (b) at various temperatures in the range of 6.0 – 1.9 K. The field-sweep rate is 0.35 kOe/sec. The insets show the plots of $H_c$ ($\odot$) and $M_r$ ($\triangle$) vs. $T$.

The $M_{mol}$ values at 50 kOe for 1c and 2c were $4.6 \times 10^4$ and $4.0 \times 10^4 \text{cm}^3\text{Oemol}^{-1}$, which were still below the saturation magnetization, $M_s$. As observed in Fig. 4, the temperature-dependent hysteresis loops relating to the field appeared below ca. 6 K and anomalous changes (steps) of the $M_{mol}$ values were observed at 0 and 29 kOe for 1c and 0 and 27 for 2c below 3 K. The observed field and temperature dependencies of $M_{mol}$ were typical behaviors for SMM. The values of the coercive force, $H_c$, and the remnant magnetization, $M_r$, were plotted as a function of temperature (inset of Fig. 4). In the $H_c$ vs. $T$ plot, the coercive force appeared at ca. 6 K, increased on cooling, and reached a plateau below 3 K. The $M_r$ vs. $T$ plot also showed a similar thermal profile. The values of $H_c$ and the remnant magnetization, $M_r$, at 1.9 K were 26 kOe and $3.1 \times 10^4 \text{cm}^3\text{Oemol}^{-1}$ for 1c and 15 kOe and $2.3 \times 10^4 \text{cm}^3\text{Oemol}^{-1}$ for 2c.

### 3.2.3. Magnetic Relaxation of 1c and 2c

In the magnetic relaxations due to $U_{eff}$ and QTM, the former are temperature-dependent and obtained by the ac magnetic susceptibility technique, while the latter are
temperature-independent and determined by the temperature dependence of the dc magnetization decay at low temperature. To determine both relaxations, therefore, the ac and dc magnetic susceptibility measurements were carried out after irradiation of 1 and 2.

3.2.3.1. Ac magnetic susceptibility measurements for 1c and 2c

Ac magnetic susceptibility measurements at a zero dc field with a 3.9 Oe ac field were carried out in the temperature range of 1.9 - 14 K. Before irradiation, no \( \chi''_{\text{mol}} \) signals (out-of-phase signal) were observed, while after irradiation, well-resolved \( \chi'_{\text{mol}} \) (in-phase signal) and \( \chi''_{\text{mol}} \) signals with frequency dependence were observed. The \( \chi'_{\text{mol}}T \) vs. \( T \) and \( \chi''_{\text{mol}} \) vs. \( T \) plots are shown in Fig. 5. In \( \chi'_{\text{mol}}T \) vs. \( T \) plot, the \( \chi'_{\text{mol}}T \) values at each frequency were constant by 30 and 24 cm\(^3\)Kmol\(^{-1}\) for 1c and 2c, respectively, until the temperature \( \chi''_{\text{mol}} \) signals appeared and then decreased below it. The constant values were consistent with those (29 and 24 cm\(^3\)Kmol\(^{-1}\) for 1c and 2c, respectively) for \( \chi_{\text{mol}}T \) in \( \chi_{\text{mol}}T \) vs. \( T \) plots (Fig. 3). As observed in Fig. 5b and 5d, \( \chi''_{\text{mol}} \) signals at each frequency showed a maximum above 6 K and the peak-top temperature shifted lower as the frequency decreased. The observations of \( \chi''_{\text{mol}} \) signals with frequency dependence indicate that the complexes 1c and 2c have a slow magnetic relaxation for reorientation of the magnetic moment.

(a)  
(b)
Fig. 5. $\chi'_\text{mol}T$ vs. $T$ and $\chi''_\text{mol}$ vs. $T$ plots for 1c (a and b) and 2c (c and d) with a 3.9 Oe ac field oscillating at given frequencies. The solid lines are a visual guide.

The value of $\Delta T_f/T_f(0)\Delta(\log w)$, where $\Delta T_f$ is the shift of the peak-temperature in $\chi'_\text{mol}$, $\log w$ is the logarithm of the applied frequency, and $T_f(0)$ is the position of the peak at zero frequency was used for the evaluation of the complex showing slow magnetic relaxation. The values obtained from the $\chi'_\text{mol}$ vs. $T$ plots for 1c and 2c were 0.24 and 0.24, respectively. According to Mydosh’s work [11], those values are in the region $\Delta T_f/T_f(0)\Delta(\log w) > 0.2$ for an SMM and supports the formation of an SMM.

3.2.3.2. dc magnetization decays measurements for 1c and 2c

To investigate the QTM pathway in the low temperature region, furthermore, the dc magnetization decays for 1c and 2c were measured after cycles of applying 50 kOe and then reducing to zero field. The decays of dc magnetizations, $M_{\text{mol}}$, were followed at various temperatures ($5.0 – 1.9$ K) in the period of $7 \times 10^3$ sec (ca. 2 hr). The data of $M$ normalized by $M_0$; $M$ at $t = 0$, for 1c and 2c were plotted as a function of time, $t$, and are shown in Fig. 6. On cooling from 5 K, the magnetization decay become slow and nearly reached the constant value of $\sim 10^5$ sec below 2.5 K, suggesting that QTM is the dominant pathway of the relaxation below 2.5 K. The temperature of 2.5 K is closed to the one at which the $H_c$ and $M_r$ values became constant in $H_c$ and $M_r$ vs. $T$ plots (inset of Fig. 4).
Fig. 6. $M/M_0$; $M_0$ is $M$ at $t = 0$, vs. time plots for 1c (a) and 2c (b) at given temperatures. The solid lines indicate the fitting results (see in the text).

Data of dc magnetization decay at given temperatures were analyzed by a stretched exponential decay (equation 1) [12].

$$M = \ln(M_0) - \left(\frac{t}{\tau}\right)^B$$

where $M_0$ is the initial magnetization, $\tau$ is the average relaxation time, and $B$ is the width of the distribution; $B = 1$ is a single-exponential decay. Taking into account the magnitude of the $M_0$ value ($M_0(T)$; $M_0$ at $T$, > 0.5$M_0$ (1.9 or 2.0 K)), in which the values of $M_0(2.0)$ for 1c and $M_0(1.9)$ for 2c were 72 and 67 %, respectively, of $M$ value at 50 kOe, the experimental decay data were selected and the data between 2.0 and 4.8 K for
1c and between 1.9 and 4.4 K for 2c were used for the fitting experiments. The \( \tau \) values of \( 5.6 \times 10^2 - 1.1 \times 10^5 \) and \( 2.8 \times 10^3 - 5.4 \times 10^5 \) sec with the \( B \) values of 0.45 – 0.58 and 0.44 – 0.49 for 1c and 2c, respectively, were obtained. The fitting results are listed in Table 3 and are shown by solid lines in Fig. 6.

Table 3
Values of \( \tau \) and \( B \) for 1c and 2c at various temperatures.

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<th>( T/K )</th>
<th>( \tau / \text{sec} )</th>
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</thead>
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<tr>
<td>2.0</td>
<td>1.1 \times 10^3 (0.45)</td>
</tr>
<tr>
<td>2.5</td>
<td>9.3 \times 10^4 (0.46)</td>
</tr>
<tr>
<td>3.0</td>
<td>7.1 \times 10^4 (0.47)</td>
</tr>
<tr>
<td>3.5</td>
<td>3.8 \times 10^4 (0.50)</td>
</tr>
<tr>
<td>3.8</td>
<td>2.8 \times 10^4 (0.49)</td>
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<tr>
<td>4.0</td>
<td>1.2 \times 10^4 (0.53)</td>
</tr>
<tr>
<td>4.2</td>
<td>5.9 \times 10^3 (0.58)</td>
</tr>
<tr>
<td>4.4</td>
<td>2.9 \times 10^3 (0.55)</td>
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<tr>
<td>4.6</td>
<td>1.3 \times 10^3 (0.52)</td>
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<tr>
<td>4.8</td>
<td>5.6 \times 10^2 (0.49)</td>
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</table>

To compare with the \( \tau \) values for 1c and 2c, the dc magnetization decays for the isomorphous complex, 3c, were also measured in the range of 1.9 – 4.4 K under the similar conditions. The decay data were fast even at 1.9 K. The value of \( M_0(1.9) \) was 4.3 \times 10^3 \text{cm}^3\text{Oe}, which was 26% of the \( M \) value at 50 kOe. The decay data at 1.9, 2.1, and 2.4 K were used and \( \tau \) values of \( 8.1 \times 10^2, 6.5 \times 10^2, \) and \( 5.8 \times 10^2 \) sec with \( B = 0.39, 0.38, \) and 0.44, at 1.9, 2.1, and 2.4 K, respectively, were obtained. (Fig. S4)

3.2.3.3. Decay time vs. \( T \) plots for 1c, 2c, and 3c

The decay data obtained from both ac and dc experiments for 1c and 2c were combined and plotted as a function of inverse \( T \), which are shown in Fig. 7. The relaxation times, \( \tau \), collected by the ac magnetic susceptibility technique and the dc magnetization decay measurements are clearly distinguishable. As shown by the solid line in Fig. 7, the magnetic relaxation time data obtained from ac measurements linearly increased on
cooling. From the Arrhenius plots; $\tau = 1/2\pi \nu = \tau_0 \exp(U_{\text{eff}}/k_B T)$, the activation energy, $U_{\text{eff}}$, for reorientation of the magnetic moment and the pre-exponential factor, $\tau_0$, were estimated to be 139 and 135 K and $1.6 \times 10^{-10}$ and $1.3 \times 10^{-10}$ sec for 1c and 2c, respectively. In addition to the Mydosh’s values ($\Delta T/T(0)\Delta(\log w) = 0.24$ for 1c and 2c), the strong frequency dependences of the $\chi'_{\text{mol}}$ and $\chi''_{\text{mol}}$ signals and the physically reasonable values of $\tau_0$ also suggest that these carbene-Co(II) complexes function as SMM rather than spin glass [13]. In contrast, the relaxation times, $\tau$, obtained by dc measurements gradually deviated from the linear line on cooling and reached a nearly constant value below 2.5 K, indicating that the decay predominantly took place in the QTM pathway. The values of lifetime, $\tau_0$, for QTM estimated from the temperature–independent dc decay were $1.1 \times 10^5$ and $5.4 \times 10^5$ sec for 1c and 2c, respectively, which correspond to the half-life time, $t_{1/2}$, of 21 and 104 hr. Observed $\tau_0$ might be due to the resonant quantum tunneling between $m_s = \pm 10/2$ [3].

To investigate the contribution of QTM pathway to the dc decay at 1.9 K for 3c, it’s Arrhenius plot [6] of ac data and the $\tau$ values at 1.9, 2.1, and 2.4 K were appended in Fig. 7a. As shown in Fig. 7a, the $\tau$ values at three temperatures were nearly constant and the value at 1.9 K largely deviated from the linear Arrhenius plot and was $8.3 \times 10^5$ times smaller than the value obtained from the extrapolation of Arrhenius plot at 1.9 K, indicating that the relaxation time at 1.9 K was strongly affected by QTM pathway. The value of $8.1 \times 10^2$ sec at 1.9 K was assigned as $\tau_0$ for 3c.
The magnetic behaviors observed after irradiation of 1 and 2 are reproducible. In annealing at 70 K, 3c showed the increase in $U_{\text{eff}}$ and $H_c$ values, [6] while 1c and 2c had no appreciable change ($U_{\text{eff}} = 135$ and 131 K and $H_c = 25$ and 15 kOe for 1c and 2c). In annealing at 100 K, on the other hand, the observed SMM behaviors disappeared by chemical decomposition of carbene and returned to the magnetic behaviors before irradiation. This result clearly indicates that the magnetic interaction between the carbene center and the cobalt ion produces the SMM.

4. Conclusion

The cyclic dinuclear complexes, 1c and 2c, showed typical SMM behaviors with $U_{\text{eff}} = 139$ and 135 K and $H_c = 26$ and 15 kOe at 1.9 K, respectively. It is worthy to note that those $U_{\text{eff}}$ values are the largest in the ones for SMM reported in the literatures and the values of the quantum tunneling time, $\tau_0$, for 1c and 2c, could be determined to be $1.1 \times 10^5$ and $5.4 \times 10^5$ sec ($t_{1/2} = 21$ and 104 hours), respectively. The molecular structure for complexes, 1 and 2, and their SMM properties after irradiation were compared with those for 3 reported previously. Three complexes had isomorphous structures and
functioned as SMM after irradiation. However, the SMM properties for 1c and 2c, which were comparable to each other, were largely different from that \( U_{\text{eff}} = 96 \, \text{K} \) and \( H_c = 10 \, \text{kOe at 1.9 K} \) [6] for 3c. Furthermore, the \( \tau_Q \) values for 1c and 2c were \( \sim 10^5 \) sec, while the lifetime of QTM for 3c was much short and the \( \tau_Q \) values was estimated to be \( 8.1 \times 10^2 \) sec. From the results of SMM properties for three complexes, the electronic effect of substituents [14] on SMM properties might be insignificant. The observed differences of \( U_{\text{eff}} \) and \( \tau_Q \) suggested that in these heterospin SMMs, the magnitude of \( U_{\text{eff}} \) and the rate of \( \tau_Q \) were closely related and the slow \( \tau_Q \) might be considered to lead large \( U_{\text{eff}} \). [1, 3(a), 15] However, the relation between the \( U_{\text{eff}} \) and \( \tau_Q \) in the heterospin SMM was not clarified by the present study. More detailed studies in the 2:2 cobalt complexes are in progress.

5. Supplementary materials

CCDC No. 803425, 734081, and 803858 for \textbf{D2py}_2(TBA), 1 and 2, respectively, contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via \url{http://www.ccdc.cam.ac.uk/conts/retrieving.html}, or from the Cambridge Crystallographic Database Centre, 12 Union Road, Cambridge, CB2 1EZ, UK; Fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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