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Heterospin single-molecule magnet behaviors after irradiation of polymorphous 2:2 cyclic diazo-cobalt(II) complexes

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ABSTRACT

Three kinds of crystals (crystals, α, β, and γ) of 2:2 cyclic cobalt complexes formulating as [Co(Br-hfpip)$_2$(**D2py$_2$**)]$_2$ X: X = 2CH$_2$Cl$_2$ (**1dα**), 4CH$_2$Cl$_2$ (**1dβ**), and 4CH$_2$Cl$_2$·4EtOH (**1dγ**) and Br-hfpip = 1,1,1,5,5,5-hexafluoro-4-(4-bromophenylimino)-2-pentanonate, were obtained and were determined to be polymorphous by X-ray crystallography, having the space groups of $P\bar{1}$ for **1dα** and **1dβ**, and $P2_1/n$ for **1dγ**. In three polymorphs, the local coordination structures of cobalt complex units in the molecule were the same; compressed octahedral. The molecular structure for **1dα** was different from those for **1dβ** and **1dγ**. The dihedral angles between the *X*–*Y* plane and the pyridine ring were 43° and 44° for **1dα** and 70–80° for **1dβ** and **1dγ**. In the crystal packings, **1dα** had a short contact between the bromo substituent in hfpip ligand and the carbon at the β position of the pyridine ring in **D2py$_2$**, while **1dβ** and **1dγ** had no short contact between the magnetically significant atoms. The powder X-ray diffraction (PXRD) patterns for the crushed samples of three polymorphs indicated that the crystal structures were changed by loosing crystal solvent and **1dα** and **1dβ** were microcrystals (**1dα'** and **1dβ'**), while **1dγ** became amorphous (**1dγ'**). In dc and ac magnetic measurements after irradiation of crushed samples (**1dα'**, **1dβ'**, and **1dγ'**), the photoproducts, **1cα'**, **1cβ'**, and **1cγ'** exhibited slow magnetic relaxation and magnetic hysteresis. **1cα'** showed a single-molecule magnet (SMM) behavior with the effective activation barrier, U_{eff}/k_B = 98 K and coercive force, H_c = 2.9 kOe at 1.9 K affected by the intermolecular antiferromagnetic interaction. **1cβ'** showed the magnetic behavior with U_{eff}/k_B = 134 K and H_c = 13 kOe at 1.9 K typical of heterospin SMM. In **1cγ'**, weak χ''_{mol} signals with frequency dependency and the temperature dependent hysteresis loop; H_c = 1.1 kOe at 1.9 K, were observed.

1. Introduction

In molecule-based magnets, single-molecule magnets [1] (SMMs) showing magnetic hysteresis and quantum tunneling magnetization (QTM) at extremely low temperatures have attracted much interest as new functional materials originating from molecules. Up to now, various single-metal complexes [2] and metal clusters[3] containing anisotropic 3d and/or 4f metal ions, and heterospin complexes [4] consisting of the spins of the anisotropic 3d and/or 4f metal ions and the 2p spins of the organic spins have been reported as SMM (or SIM; single-ion magnet). In our heterospin systems [5–7], the organic spin centers, which were far from the binding site, interacted with the metal ion through the aromatic ligands. Therefore, various combinations of organic spin with the metal ions were available. The combination of a high-spin cobalt(II) ion and the pyridine-carbene [5] and –aminoxyl [5d,6] ligands provided unique heterospin SMMs with a large effective activation barrier (U_{eff}/k_B) for reorientation of the magnetic moment and with a magnetic hysteresis having a large coercive force (H_c) above 1.9 K. Actually, the cyclic 2:2 cobalt–carbene complexes [7] after irradiation of [Co(I-hfpip)$_2$(**D2py$_2$-*tert*-Bu**)]$_2$; I-hfpip = 1,1,1,5,5,5-hexafluoro-4-(4-iodophenylimino)-2-pentanonate and **D2py$_2$-*tert*-Bu** = 5-(*tert*-butylethynyl)-1,3-phenylenebis(4-pyridyldiazomethane), showed SMM behaviors with extra large values of U_{eff}/k_B = 139 K, and H_c = 26 kOe at 1.9 K, in addition to the temperature independent QTM relaxation times τ_Q of 1.1 × 10^5 s. Recently, we reported the role of organic spin in heterospin SMM. The organic spin interacted with anisotropic cobalt ion to depress the QTM time, leading to the formation of heterospin SMM with large U_{eff} and H_c values [5a]. To understand the structural factors affecting heterospin SMM properties, this time, the magnetic properties of crystal polymorphs of heterospin Co complexes were investigated. Crystal polymorphs being the same molecule with different molecular structures and arrangements in the crystalline state [8], have been extensively used in the field

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of solid-state emission materials. Since the solid-state emission behavior is intensively affected by the molecular structure and arrangement in the solid state, strategies taking advantage of crystal-to-crystal (C-to-C) phase transitions in polymorphs are a promising approach to molecules showing the emission alteration induced by external stimuli [9]. Many studies on the polymorph-dependent emissions have been reported [10,11]. The magnetic property of SMM also depended on the molecular structure and arrangement in the crystalline state. Therefore, the crystal polymorphs of heterospin complexes might allow us to reveal the relationship between the structures and the magnetic properties. Flexible organic molecules and metal complexes have been reported to produce many crystal polymorphs [8]. Since our heterospin system used a flexible organic ligand having unpaired electrons, the obtained heterospin complexes were expected to have crystal polymorphs. During the studies on SMMs, we found that the combination of **D2py$_2$**; 5-bromo-1,3-phenylenebis(4-pyridyldiazomethane) and Co(Br-hfpip)$_2$ afforded three crystal polymorphs containing crystal solvents formulated as [Co(Br-hfpip)$_2$(**D2py$_2$**)]$_2$X: X = crystal solvent. The obtained three polymorphs showed different magnetic behaviors under similar conditions. We herein report the crystal structures for crystal polymorphs of [Co(Br-hfpip)$_2$(**D2py$_2$**)]$_2$ X and their magnetic behaviors after irradiation (see Scheme 1).

2. Experimental

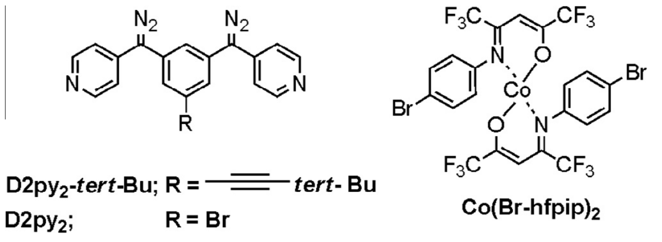
2.1. General methods

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 at the Analytical Center of the Faculty of Science at Kyushu University.

2.2. X-ray molecular and crystal structure analyses

Suitable single crystals were glued onto a glass fiber using epoxy resin. All single-crystal X-ray diffraction (SXRD) data were collected on a Rigaku R-AXIS RAPID and a Bruker AXS APEX-II diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71069 Å). The molecular structures were solved by direct methods (SIR 92 [12]). The refinements were converged using the full-matrix least squares method from the Crystal Structure software package [13]. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined isotropically. Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publications no. CCDC-1013615, -1013616, and -1013617 for **1dα**, **1dβ**, and **1dγ**, respectively.

Powder X-ray diffraction (PXRD) spectra were obtained with a Bruker AXS D2PHASER. PXRD measurements for the crystal and powder samples were carried out at a 2θ angle of 5–35° at 25 °C.



Scheme 1. Formula of **D2py$_2$-*tert*-Bu**, **D2py$_2$**, and Co(Br-hfpip)$_2$.

2.3. SQUID measurements

Direct current (dc) and alternating current (ac) magnetic susceptibility data were obtained with a Quantum Design MPMS5S SQUID magneto/susceptometer, respectively, and corrected for the magnetization of the sample holder and cellophane tape, and for diamagnetic contributions to the samples, which were estimated from Pascal's constants [14]. The ac magnetic susceptibility measurements were carried out with a 3.9 Oe oscillating field and a zero dc field at frequencies of 1–997 Hz. In our irradiation system [15] for photolysis of diazo chromophore inside SQUID apparatus, the largest amount of sample for effective photolysis of diazo-cobalt complex was less than 1 mg. In such small amounts of spins, 10 and 30 K before and after irradiation, respectively, were the highest temperature at which it was possible to measure the paramagnetic susceptibility.

2.4. Materials

The pyridine-diazo derivative, **D2py$_2$**, and the complex, Co(Br-hfpip)$_2$, were prepared by procedures reported previously [5d,7,16,17].

[Co(Br-hfpip)$_2$(D2py$_2$)]$_2$: A solution of Co(Br-hfpip)$_2$ (55 mg, 0.08 mmol) in CH$_2$Cl$_2$ (2 mL) and a solution of **D2py$_2$** (30 mg, 0.08 mmol) in CH$_2$Cl$_2$ (2 mL) were mixed and to this was added acetonitrile, *n*-hexane, or EtOH (2 mL) for **1dα**, **1dβ**, and **1dγ**, respectively. The solution mixture was kept at 4 °C for 1 week. Crystal **1dα** was obtained as red block crystals. m.p. (dec.) 140–145 °C, IR (KBr) $\nu_{=N2}$ 2063 cm^{-1}. *Anal.* Calc. for $C_{80}H_{42}N_{16}O_4F_{24}Br_6Co_2 \cdot 0.8CH_2Cl_2$: C, 40.23; H, 1.82; N, 9.29. Found: C, 40.53; H, 2.01; N, 9.01%. Crystal **1dβ** was obtained as red block crystals. m.p. (dec.) 145–150 °C, IR (KBr) $\nu_{=N2}$ 2061 cm^{-1}, *Anal.* Calc. for $C_{80}H_{42}N_{16}O_4F_{24}Br_6Co_2 \cdot 0.2CH_2Cl_2$: C, 40.79; H, 1.81; N, 9.49. Found: C, 41.12; H, 2.29; N, 9.00%. Crystal **1dγ** was obtained as red block crystals. m.p. (dec.) 115–120 °C, IR (KBr) $\nu_{=N2}$ 2059 cm^{-1}, *Anal.* Calc. for $C_{80}H_{42}N_{16}O_4F_{24}Br_6Co_2 \cdot EtOH$: C, 41.20; H, 2.02; N, 9.37. Found: C, 41.00; H, 1.89; N, 9.04%.

3. Results and discussion

3.1. Preparations

Didiazo-dipyridine derivative, **D2py$_2$**, which produces the quintet carbene with S = 4/2 after irradiation, was prepared by the procedure reported previously [15]. The bidentate chelating cobalt complex, Co(Br-hfpip)$_2$; Br-hfpip = 1,1,1,5,5,5-hexafluoro-4-(4′-bromphenylimino)-2-pentanonate, was prepared in a manner similar to the modified procedure for the unsubstituted one [5d,17]. The solutions of **D2py$_2$** and Co(Br-hfpip)$_2$ in CH$_2$Cl$_2$ were mixed at a 1:1 molar ratio and the same amounts of organic solvents (CH$_3$CN, *n*-hexane, and EtOH) were added. The solutions were left at 4 °C for 1 week. Three kinds of single crystals, α, β, and γ, were obtained as red blocks from the mixed solutions after adding CH$_3$CN, *n*-hexane, and EtOH, respectively. The obtained single crystals were labile under ambient atmosphere. Especially, the crystal γ was readily destroyed by loosing crystalline solvents, CH$_2$Cl$_2$ and EtOH, to become amorphous.

3.2. Crystal structure analysis

Single crystals, α, β, and γ, were analyzed by single-crystal X-ray diffraction (SXRD). The crystallographic data and experimental details are listed in Table S1. Crystal α, β, and γ were the ones of the complexes formulating as **[Co(Br-hfpip)$_2$(D2py$_2$)]$_2$** (**1d**). Crystals, **1dα**, **1dβ**, and **1dγ**, contained two molecules of CH$_2$Cl$_2$, four