Magnetic behavior of tetrakis[4-(*N-tert*-butyl-*N*-oxylamino)pyridine]bis(isocyanato-*N*)cobalt(II) in frozen solution†

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A complex of cobalt(II)(OCN)₂ coordinated with four pyridines having a stable *tert*-butyl aminoxyl exhibited in frozen MTHF a slow magnetic relaxation for the reorientation of magnetization with activation barrier, $\Delta/k_B = 50$ K, and a hysteresis loop having a fast relaxation at 0 Oe below 2.5 K.

For the construction of single-molecule magnets (SMM)[1] exhibiting slow magnetic relaxation, we proposed the heterospin systems consisting of 3d spins of the metal ions and 2p spins of unpaired electrons of organic radicals in frozen solutions.[2,3] The metal ion and the high-spin organic species are designed to contribute mainly to the large zero-field splitting, *D,* and high spin quantum number, *S*, respectively, and the complex should be magnetically isolated under a frozen solution condition. Actually, a 1 : 4 complex of Co(SCN)₂ and diazo(4-pyridyl)phenylmethane in frozen solution after irradiation exhibited SMM-like magnetic behavior with an activation barrier, $\Delta/k_B = 89$ K.[2] This was the first example of a monometallic SMM. To improve the thermal stability of organic spin and develop our heterospin SMMs further, a persistent *tert*-butyl aminoxyl that has been well studied for magnetic coupling with metal ions,[4] was employed as an organic spin source. Herein, we report the magnetic properties of the complex of high-spin cobalt(II), Co(OCN)₂, coordinated with 4-(*N-tert*-butyl-*N*-oxylamino)pyridine, 4NOPy, in frozen solution investigated by a SQUID magneto/susceptometry.

The crystalline cobalt(II) complex, [Co(OCN)₂·(4NOPy)₄], was obtained as dark red bricks from a solution of the mixtures Co(NO₃)₂–KNCO in EtOH and 4NOPy in Et₂O at −14 °C. The molecular structure of [Co(OCN)₂·(4NOPy)₄] was shown by X-ray crystal structure analysis‡ (Fig. 1) to be octahedral. In the crystal packing, the short distances with the neighboring molecules were observed between the aminoxyl radical center and C of the pyridine ring (O2–C4′ = 3.157 Å). These short contacts would lead to intermolecular antiferromagnetic interactions in the crystalline state of the complex. In the $\chi_{mol}T$ *vs. T* plot obtained by the dc magnetic susceptibility measurement for the microcrystalline sample of [Co(OCN)₂·(4NOPy)₄], a steep decrease of $\chi_{mol}T$ values below 30 K was indeed observed, which is due to intermolecular antiferromagnetic interactions. In order to eliminate intermolecular interactions, the dc and ac magnetic measurements of the complexes in frozen solutions were carried out. Solutions (10 mM, 150 µl) of the crystal of [Co(OCN)₂·(4NOPy)₄] dissolved in 2-methyltetrahydrofuran (MTHF) were used as samples.§ From the comparison of thermal profile of $\chi_{mol}T$ values for crystalline and frozen solution samples, it is confirmed that the intermolecular antiferromagnetic interaction was effectively eliminated and the complex was magnetically isolated by employing frozen solution condition as expected (Fig. S2†).

The ac magnetic susceptibility data for a frozen solution sample of [Co(OCN)₂·(4NOPy)₄] were measured in a zero dc field with a 5.0 Oe ac field and in the temperature range of 1.9–10 K. In the complex, well-resolved χ' and χ'' signals (in-phase and out-of-phase components of the ac magnetic susceptibilities, respectively) with a frequency dependence were observed, indicating that the complex has a slow magnetic relaxation for flipping the spin. In the $\chi'T$ *vs. T* plots (Fig. 2a), the values of $\chi'T$ were nearly constant (8.7–8.5 emu K mol⁻¹) until the onset of the contribution of out-of-phase χ'' signals. The value of 8.5 emu K mol⁻¹ is much larger than the one calculated by the spin-only equation (3.5) with four isolated aminoxyls (0.375 × 4) and one high-spin cobalt(II) ion (2.0 × 1), suggesting that aminoxyl and cobalt ion in the complex interact ferromagnetically to form the high-spin ground state with $S = 5/2$ and $g = 2.8$ (assuming the effective $S' = 1/2$ for cobalt(II) ion which was obtained by an EPR study on [Co(SCN)₂·(Py)₄]). As observed in the χ'' *vs. T* plot (Fig. 2b), χ'' signals at each frequency show a maximum above 1.9 K and a peak-top temperature that is shifted to lower emu mol⁻¹ as the frequency decreases. In addition to the main peak, a small peak (shoulder) due to a minor component formed under the experimental conditions was observed in the lower temperature region. Since each frequency at the peak-top temperature for χ'' is consistent with $1/\tau$, the activation energy, Δ/k_B, for flipping the spin and the relaxation time, τ_0, were estimated from the Arrhenius plot: $\tau = \tau_0 \exp(\Delta/k_BT)$ to give $\Delta/k_B = 50$ K and $\tau_0 = 1.8 \times 10^{-7}$ s. In more detailed ac magnetic susceptibility experiments, a symmetrical Cole–Cole diagram was obtained, indicating that there is only one magnetization relaxation process present for this complex (Fig. S3†).

The variable-field magnetization (M_{mol}) of the frozen solution sample was measured at 1.9–5.0 K in the range 0–50 kOe. Typical
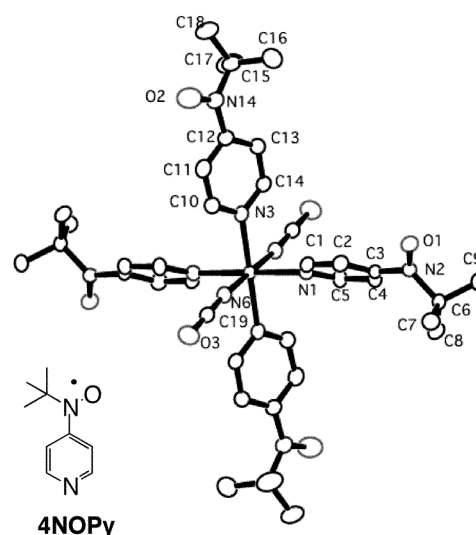
Fig. 1 ORTEP drawing of the molecular structure of [Co(OCN)₂·(4NOPy)₄]. Hydrogen atoms and a molecule of Et₂O were omitted for the sake of clarity.

large deviations from the Brillouin function in the plots of $M_{mol}/N\mu_B$ *vs.* H/T (Fig. S4a†), show that the complex has a large magnetic anisotropy. The experimental data were analyzed on the basis of the ligand field theoretical model including spin–orbit coupling, superexchange interactions between Co and radicals, uniaxial ligand field, and the Zeeman interaction. The energy level scheme obtained (Fig. S4c†), provides a thermodynamic activation barrier U of 60 K. The large difference between the kinetic barrier (U_{eff}) and thermodynamic barrier (U) for flipping the spin can be explained by the contribution of a quantum tunneling effect.

A magnetization hysteresis loop of the frozen solution sample was also measured with a sweep rate of 0.035 T s^{-1} at five temperatures in the range 1.9 (Fig. 3)–3.0 K. The hysteresis loop appeared below *ca.* 2.5 K and the area within the loop increased with decreasing temperature. The M_{mol} value sigmoidally increases in the range 0–5 kOe on increasing the applied field from 0 to 50 kOe, and abruptly decreases near 0 Oe when the applied field is reduced from 50 to 0 kOe (the inset of Fig. 3). In negative field, similar behavior of the M_{mol} value was observed with a negative sign. The shape of the observed hysteresis loop might be due to a fast magnetization relaxation¶ at 0 Oe and the effect of minor
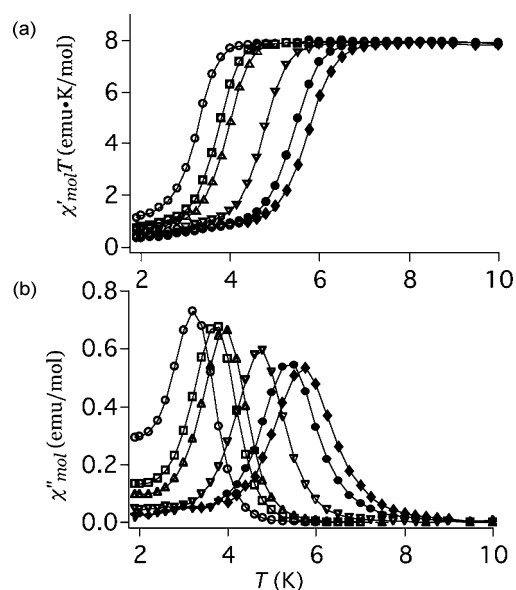
component(s) contained under experimental conditions.[5,6] Taking the result of ac experiments into account, however, the contribution of the latter might be small.

Similar magnetic behavior showing slow magnetic relaxation was observed in an analogous bis(thiocyanato)cobalt(II)-pyridine complex, [Co(SCN)$_2$·(4NOPy)$_4$], under similar conditions, in which the activation barrier is found to be 30 K. (Fig. S5†) This result is noteworthy; the activation barrier for flipping the spin in these spin systems can be controlled by the axial ligands. Since the results of ac and dc magnetic experiments are perfectly reproducible and those for 5 and 15 mM samples under similar conditions show no significant difference with the 10 mM sample, these experiments, in addition to the difference of χ values below 10 K between crystalline and frozen solution samples, may rule out the possibility that an aggregation of the complex could lead to the observed slow relaxation of magnetization. Although it is difficult to obtain direct information on the structure of [Co(OCN)$_2$·(4NOPy)$_4$] formed in frozen solution, the origin of the observed magnetic behavior may be safely concluded to be due to one isolated molecule of the cobalt complex. The strong frequency dependence of the χ' and χ'' signals and the physically reasonable value of τ_0 suggest that the Co complex in frozen solution functions as an SMM rather than a spin glass.[7] More detailed analysis of the magnetic properties and structure of the complex formed in frozen solution are in progress.

Fig. 2 (a) $\chi'T$ *vs.* T and (b) χ'' *vs.* T plots for [Co(OCN)$_2$·(4NOPy)$_4$] in MTHF with a 5 Oe ac field oscillating at 1000 (♦), 500 (●), 100 (▽), 10 (△), 5(□), and 1(○) Hz. The solid lines are visual guides.
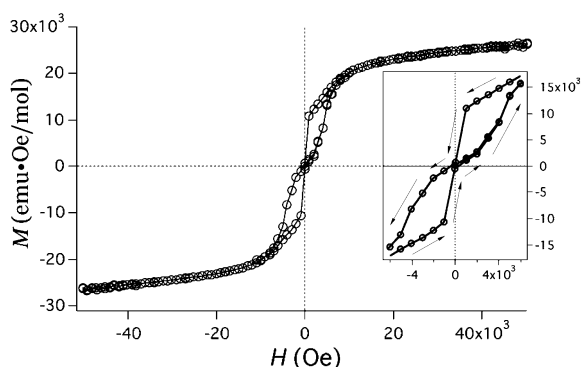
Notes and references

‡ Crystal data for [Co(OCN)$_2$·(4NOPy)$_4$]: red blocks (0.3 × 0.3 × 0.2 mm) C$_{38}$H$_{52}$N$_{10}$O$_6$Co·Et$_2$O, M_r = 877.95, monoclinic, space group $P2_1/c$ (no 14) a = 11.892(4), b = 18.244(7), c = 11.950(3) Å, β = 115.81(2)°, V = 2333.7(1) Å^3, Z = 2, d_c = 1.249 g cm^{-1}, T = 123 K, 21554 reflections measured, 5338 unique reflections (R_{int} = 0.109), refinement with 577 parameters converged with agreement factors R_1 ($I > 2\sigma(I)$) = 0.049, wR_2 = 0.140($I > 1\sigma(I)$), GOF = 0.64. CCDC 224808. See http://www.rsc.org/suppdata/cc/b4/b403524k/ for crystallographic data in .cif or other electronic format.

§ To investigated the coordination structure in solution, the UV–Vis spectrum of the solution of [Co(OCN)$_2$·(4NOPy)$_4$] in MTHF was measured in the temperature range 160–295 K (Fig. S1†).

¶ The dc magnetization decay was followed after a cycle of increasing the applied field from 0 to 10 kOe and then reducing the applied field from 10 to 0 kOe. The decay data at 1.9 K were analyzed by the extended exponential equation to give the decay rate ~ 1.2 × 10^{-2} s^{-1}.

1 D. Gatteschi and R. Sessoli, *Angew. Chem., Int. Ed.*, 2003, **42**, 268.
2 S. Karasawa, G. Zhou, H. Morikawa and N. Koga, *J. Am. Chem. Soc.*, 2003, **125**, 13676.
3 (*a*) S. Karasawa, H. Kumada, N. Koga and H. Iwamura, *J. Am. Chem. Soc.*, 2001, **123**, 9685; (*b*) S. Karasawa and N. Koga, *Polyhedron*, 2003, **22**, 1877; (*c*) H. Morikawa, S. Karasawa and N. Koga, *Appl. Magn. Reson.*, 2003, **23**, 507; (*d*) S. Karasawa and N. Koga, *Polyhedron*, 2001, **20**, 1387.
4 Y. Ishimaru, M. Kitano, H. Kumada, N. Koga and H. Iwamura, *Inorg. Chem.*, 1998, **37**, 2273–2280.
5 (*a*) D. N. Hendrickson, G. Christou, H. Ishimoto, J. Yoo. E. K. Brechin, A. Yamaguchi, E. M. Rumberger, S. M. J. Aubin, Z. Sun and G. Aromi, *Polyhedron*, 2001, **20**, 1479; (*b*) S. M. J. Aubin, N. R. Dilley, M. W. Wemple, M. B. Maple, G. Christau and D. N. Hendrickson, *J. Am. Chem. Soc.*, 1998, **120**, 839.
6 K. Takeda, K. Awaga, T. Inabe, A. Yamaguchi, H. Ishimoto, T. Tomita, H. Mitamura, T. Goto, N. Mori and H. Nojiri, *Phys. Rev. B*, 2002, **65**, 94424.
7 J. A. Mydosh, *Spin Glasses; An Experimental Introduction*, Taylor and Francis, London, 1993.

Fig. 3 Field dependence of magnetization at 1.9 K for [Co(OCN)$_2$·(4NOPy)$_4$] in MTHF. The inset shows the field range of ±5 kOe. Arrows show the direction of the change of M_{mol} value, when the field changes ±50 kOe.