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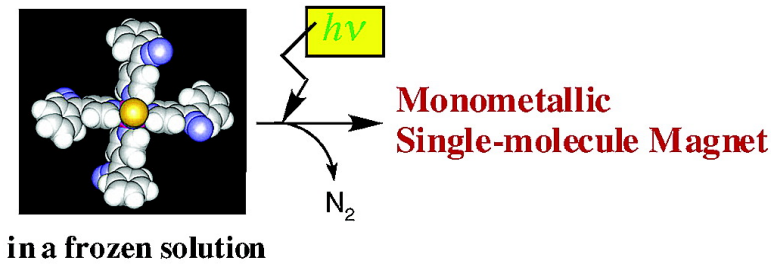


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# Magnetic Properties of Tetrakis[4-(α-diazobenzyl)-pyridine]bis(thiocyanato-*N*)cobalt(II) in Frozen Solution after Irradiation. Formation of a Single-Molecule Magnet in Frozen Solution

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Single-molecule magnets[1] exhibiting slow spin relaxation are of great interest not only in molecule-based magnets but also in the development of functional nanosized materials in general. We have been studying the magnetic properties of heterospin systems[2] consisting of the 3d spins of metal ions and the 2p spins of a set of carbenes with $S = {}^2/_2-{}^{10}/_2$[3]. A molecular cluster formed from a 3:2 mixture of bis(hexafluoro-acetylacetonato)copper(II) and tripyridyl-tridiazo derivative in frozen solution, for example, exhibits spin-glasslike magnetic behavior after irradiation.[4] These magnetic studies of our heterospin systems lead to the idea of the construction of a single-molecule magnet in which the metal ion and the high-spin carbene contribute to large *D* and *S* values, respectively. For this purpose, $Co(SCN)_2$ in which a high-spin cobalt (II) ion is known to have relatively large magnetic anisotropy and the simplest carbene, (4-pyridyl)phenylcarbene **1c**, with a triplet ground state were selected.

The 4-(α-diazobenzyl)pyridine, **1**, was prepared by a procedure reported previously.[5] Crystalline complex $Co(SCN)_2 \cdot \mathbf{1}_4$ was obtained as red bricks from a solution of a 1:4 molar mixture of $Co(SCN)_2$ and **1** in ethanol at room temperature. Its molecular structure was revealed by a single-crystal X-ray analysis[6] to be octahedral with a center of symmetry at the cobalt ion (Figure 1). The cobalt ion is coordinated with six nitrogen atoms of four pyridine rings and two SCN ions in the distance of 2.106−2.200 Å. The SCN ions are coordinated in a trans configuration.

Because it was difficult to generate the carbene centers quantitatively by direct irradiation of the crystalline complex and extract the magnetic properties of an assembly of the single complex molelcules free from intermolecular magnetic interaction, the magnetic properties before and after irradiation of a 1:4 mixture of $Co(SCN)_2$ and **1** in a frozen solution were investigated by SQUID magneto/susceptometry.

The UV−vis spectrum of the 1:4 mixture (2 mM) of $Co(SCN)_2$ and **1** in MTHF−EtOH at room temperature showed two sets of broad absorptions at 610 and 625 nm, and at 484 nm. The former absorptions are characteristic of the d−d transitions of the cobalt-(II) ion in a tetrahedral structure. Any absorption due to the octahedral structure was not clear from the contribution of the n−$\pi$* transition (500 nm) of diazo moieties. On cooling to 175 K, the absorption for the former gradually decreased and disappeared at 190 K, while the latter increased and slightly shifted with an isospecific point at 520 nm. The observed temperature dependence of the spectra suggested that the tetrahedral form shifted to the octahedral form. At 175 K, only a broad absorption at 480 nm was observed. Therefore, the 1:4 mixture of $Co(SCN)_2$ and **1** in frozen solution[7,8] is safely considered to be the octahedral complex having the structure shown in Figure 1.

The ac and dc magnetic susceptibility data were obtained before and after irradiation of the 1:4 mixture of $Co(SCN)_2$ and **1** (10 mM/50 $\mu$L) in MTHF−EtOH. Photolysis of the sample was performed in SQUID apparatus through an optical fiber[9] and followed by magnetization ($M_{mol}$) measurements at 5 kOe at 5 K. When the irradiation started, the $M_{mol}$ values gradually developed and leveled off after ca. 30 h.

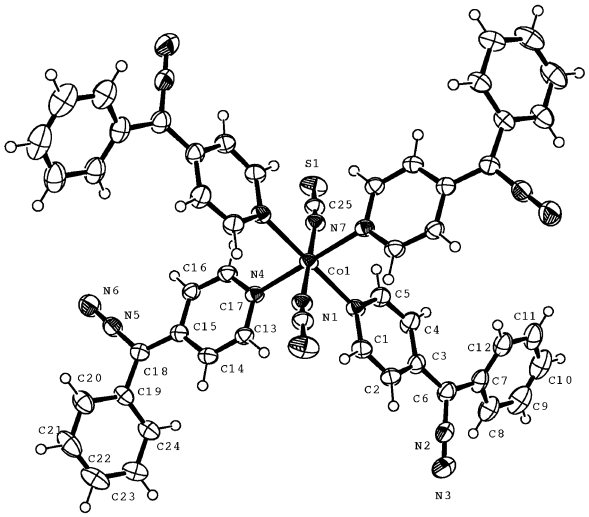


***Figure 1.*** ORTEP drawing of the molecular structure of $[Co(SCN)_2 \cdot \mathbf{1}_4]$.

The ac magnetic susceptibility measurements were performed in a zero dc field with a 5.0 Oe ac field at the frequency of 1000, 500, 100, 10, and 1 Hz in the temperature range of 2.0−10 K. Before irradiation, any magnetic behavior of the slow spin relaxation was not observed. After irradiation, on the other hand, both in-phase and out-of-phase components, $\chi'$ and $\chi''$, respectively, of the ac magnetic susceptibility showed frequency dependence. The plots of $\chi'T$ versus $T$ and $\chi''$ versus $T$ before and after irradiation are shown in Figure 2a and b, respectively. In the plot of $\chi'T$ versus $T$, in-phase $\chi'T$ values before irradiation are ∼2 emu K mol$^{-1}$ in the temperature range of 2−7 K, while the values after irradiation are 11.0 emu K mol$^{-1}$ at 10 K and remain essentially constant on cooling until 5−7 K. The value at 10 K is clearly larger than 6 emu K mol$^{-1}$ calculated by a spin-only equation with the isolated carbenes and cobalt(II) ion ($\chi'T = 2$, which is the value before irradiation, is used for Co(II) ion), suggesting that the carbenes generated by photolysis interact with cobalt(II) ion ferromagnetically. Below 5 K, $\chi'T$ values decreased depending on the frequency. As observed in Figure 2b, the signals due to $\chi''$ showed two maxima at each frequency. Especially, two maxima were clearly observed in 1 Hz signals at 2.8 and 4.0 K. This double relaxation suggested the presence of two components (A and B in which $\Delta/k_B$ for A is larger) under the experimental conditions. As each frequency at the peak-top temperature for $\chi''$ is consistent with $1/\tau$, the activation


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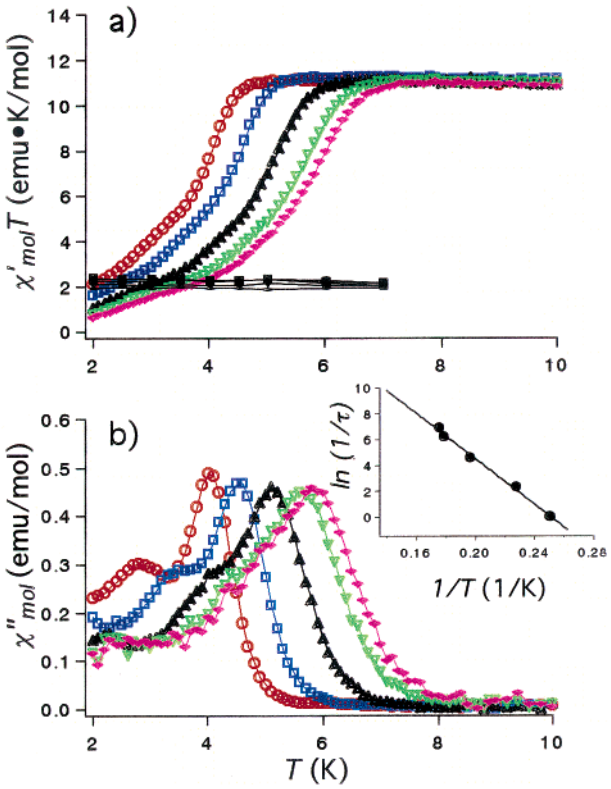


***Figure 2.*** Plots of (a) $\chi'T$ versus $T$ and (b) $\chi''$ versus $T$ obtained after irradiation of a 1:4 mixture (10 mM) of $Co(SCN)_2$ and **1** in frozen MTHF−EtOH solution with a 5 Oe ac field oscillating at 1000 (◆), 500 (▽), 100 (△), 10 (□), and 1 (○) Hz. The solid lines are visual guides. The black filled marks in (a) are the data before irradiation, and the inset in (b) is an Arrhenius plot for the component A.

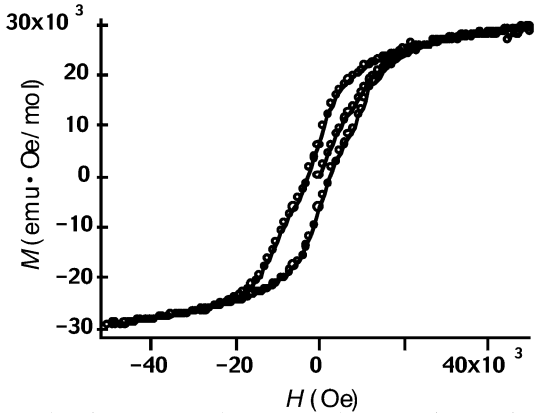


***Figure 3.*** Plot of a hysteresis loop obtained at 2 K after irradiation of a 1:4 mixture of $Co(SCN)_2$ and **1** in frozen MTHF−EtOH solution with a sweeping rate of 0.35 kOe/s.

energy, $\Delta/k_B$, for flipping the spin and the relaxation time, $\tau_0$, were obtained from Arrhenius plots, $\ln(1/\tau)$ versus $1/T$; $\Delta/k_B = 89$ (50) K and $\tau_0 = 2.3 \times 10^{-10}$ ($3.2 \times 10^{-10}$) s. The values in parentheses are for component B.

The dc magnetization[10] was measured in the range −50 to 50 kOe with a field-sweeping rate of 0.35 kOe/s. The cobalt complex exhibited a hysteresis with respect to the applied field below ca. 3.5 K; the hysteresis loops increased with decreasing temperature.[11] The plot of hysteresis loop at 2 K is shown in Figure 3. Coercive force and remnant magnetization at 2 K are ca. 3.0 kOe and $6.5 \times 10^3$ emu Oe $mol^{-1}$, respectively. The decays of magnetization were followed after cycles of applying 10 kOe and then reducing to the zero field. The dc magnetization decay data were collected at nine temperatures in the 3.4−1.9 K range and analyzed by the extended exponential equation. The dc decay rates which are ca. $2 \times 10^{-3}$ $s^{-1}$ are nearly constant in the temperature range of 2.7−1.9 K.[12]

When the irradiated sample was annealed at 70 K, the observed dc and ac magnetic signals completely disappeared and the magnetic behavior returned to that before irradiation.

Although the difference of components A and B observed in the ac measurement is not clear at the present stage, the observations of the frequency dependence of $\chi''$ and of a hysteresis loop at 2 K in ac and dc measurements, respectively, suggest that this cobalt−carbene complex functions as a single-molecule magnet. The combination of the high-spin organic radicals and the magnetically anisotropic metal ions will lead to the development of a new type of single-molecule magnets of nanometer size. Systematic changes of $S$ values of carbenes together with theoretical analyses are in progress.

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**Supporting Information Available:** Crystallographic details (CIF) for $[Co(SCN)_2 \cdot \mathbf{1}_4]$, UV−vis spectra (S1), and the dc magnetization decay and $\ln(1/\tau)$ versus $1/T$ plot (S2a and S2b, respectively) (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(6) Crystal data for $[Co(SCN)_2 \cdot \mathbf{1}_4]$; red blocks (0.5 mm × 0.5 mm × 0.5 mm) $C_{50}H_{36}N_{14}S_2Co$, $M = 955.98$, monoclinic, space group $P2_1/c$ (No. 14), $a = 10.367(6)$ Å, $b = 11.437(6)$ Å, $c = 19.44(1)$ Å, $\beta = 102.35(3)°$, $V = 2252.1(2)$ Å$^3$, $Z = 2$, $D_c = 1.41$ g cm$^{-1}$, $T = 123$ K, $\mu$ (Mo K$\alpha$) = 5.28 cm$^{-1}$, 20 744 reflections measured, 5139 unique reflections ($R_{int} = 0.047$), refinement with 322 parameters converged with agreement factors $R_1$ ($I > 2\sigma$) = 0.039, w$R_2$ = 0.081($I > 2\sigma$), GOF = 1.09.

(7) An EPR spectrum of the 1:4 mixture of $Co(SCN)_2$ and **1** in frozen solution before irradiation at 6.5 K is comparable to that reported previously for the high-spin Co(II) having the ground state with an effective spin of $S' = {}^1/_2$.

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(10) Diamagnetic susceptibility ($\chi_{dia}$) for a solvent and a capsule in dc measurements was −1.7 to $-1.8 \times 10^{-3}$ emu at 50 kOe, which is 12−13% of the $M$ value after irradiation.

(11) The shape of the hysteresis loop also depends on the sweeping rate of the field.

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