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Magnetic Behavior of a 3:2 Mixture of Bis(hexafluoroacetylacetonato)copper(II) and 1,3,5-Benzenetriyltris(4-pyridyldiazomethane) in a Frozen Solution after Irradiation: Photochemical Formation of a Solid Solution Magnet

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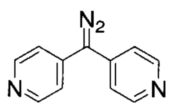
For the construction of a molecular magnet, it is required to assemble as many spins as possible in the two and three-dimensional mesoscopic network and couple them in a ferro- or ferrimagnetic fashion.[1] We have employed a strategy of constructing heterospin systems consisting of 3d metal and free radical 2p spins.[2,3] The 1:1 mixed ligand complexes, $[\mathrm{Mn(hfac)_2}\cdot\mathbf{1}]_n$ and $[\mathrm{Cu(hfac)_2}\cdot\mathbf{1}]_n$, of bis(hexafluoroacetylacetonato)manganese(II) and copper(II), $\mathrm{Mn(hfac)_2}$, and $\mathrm{Cu(hfac)_2}$, coordinated with a photoresponsive magnetic coupler, diazodi(4-pyridyl)methane **1**, formed one-dimensional chains and gave ferri- and ferromagnetic super high-spin molecules with $S = 317$ (at 1.9 K)[2b] and 34 (at 3.0 K),[3a] respectively, after generation of the carbene centers by photolysis of the diazo moieties in the complexes. To increase the dimension of the spin-networks from 1D to 2D and 3D structures, two approaches can be considered; one is the use of coordinatively highly unsaturated metal ion without hfac ligand, and the other is the design of highly branched base ligand. On the basis of the latter strategy, 1,3,5-benzentriyltris(4-pyridyldiazomethane) **2** was designed and prepared as a novel photoresponsive magnetic coupler. In this paper,[4] we report the magnetic behavior after photolysis of the 3:2 molar mixture of $\mathrm{Cu(hfac)_2}$ and **2** *in frozen solutions*.[5]



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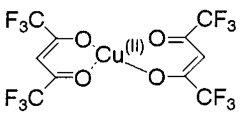
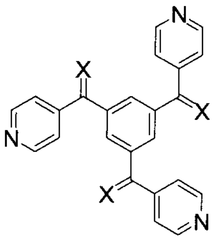


Cu(hfac)$_2$



2 ; X = N$_2$
2c ; X = ••

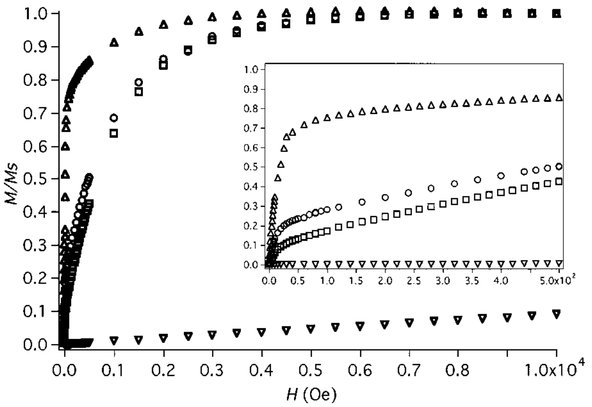


Figure 1. M/M_s vs H plots at 2 K after irradiation of 3:2 mixtures of $\mathrm{Cu(hfac)_2}$ and **2** in 5(□), 10 (○), and 20 (△) mM concentrations in frozen solutions together with the data (▽) before irradiation of a 20 mM sample. The low-field region (<0.5 kOe) is enlarged in Inset.

Triketone derivative was prepared by trilithiation of 1,3,5-tribromobenzene with *n*-butyllithium followed by the reaction with 4-formylpyridine and then the oxidation with activated manganese(IV) dioxide. The carbonyl groups were converted to the diazo groups by a standard procedure reported previously.[2,3] The tridiazo-tripyridyl derivative **2** was recrystallized from $\mathrm{CHCl_3}$ to afford red plates. The crystal and molecular structure of **2** was revealed by X-ray structure analysis.[4] Carbene **2c** generated by photolysis of **2** was confirmed to be a ground-state septet by EPR spectrum and magnetization measurement under the conditions similar to the ones for the following experiments on the complex. Each carbene center was also expected to interact ferromagnetically with copper(II) ions through the pyridine rings in the complex with $\mathrm{Cu(hfac)_2}$.[3a,c]

The magnetic properties before and after photolysis of self-assemblies consisting of $\mathrm{Cu(hfac)_2}$ and **2** were studied by means of SQUID magneto/susceptometer. In these experiments, 50 μL of solutions of $\mathrm{Cu(hfac)_2}$ in MTHF and **2** in MTHF−$\mathrm{CH_2Cl_2}$ (4:1) by 3:2 molar ratio were employed as the sample for SQUID measurements.[6] The light from an argon ion laser ($\lambda = 514$ nm) was used, and the irradiation of the sample was performed in a sample room inside SQUID apparatus. Photolysis of the samples was confirmed to take place quantitatively by taking the difference of absorptions at 492 nm due to the diazo moieties before and after SQUID measurements. Saturation magnetization values (M_{sat}) obtained from the following experiments ranged 92.4−95.7% of the theoretical ones.

Magnetization data, M_{mol}[7] before and after irradiation of the 3:2 mixtures of $\mathrm{Cu(hfac)_2}$ with **2** in 5, 10, and 20 mM concentrations were measured at 2 and 5 K in the field range 0−10 kOe. Before irradiation, the magnetization data exhibited a large contribution due to diamagnetic solvents.[8] When the irradiation started, the M_{mol} values at 5 K gradually developed and leveled off after 2 h. The M_{mol} versus H plots at 2 K before and after irradiation of the 3:2 mixtures in various concentrations are shown in Figure 1.

The magnetization curves were analyzed to consist at least of two components, fast and slow saturating fractions (FF and SF, respectively). The amounts of FF observed in low-field region

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[6] (6) In the UV−vis spectrum of a 3:2 mixture (5 mM) at room temperature, the shift of the absorption from 492 to ∼480 (shoulder) nm due to n−π^* transition of diazo moiety was observed.

[7] (7) The formula weight of 3:2 complex, $[(\mathrm{Cu(hfac)_2})_3\cdot\mathbf{2}_2]$, was used.

[8] (8) The value of χ_{dia} was estimated to be -4.76×10^{-4} emu·Oe from M vs H plot before irradiation and it was negligibly small (<0.7%) in the experimental data after irradiation.

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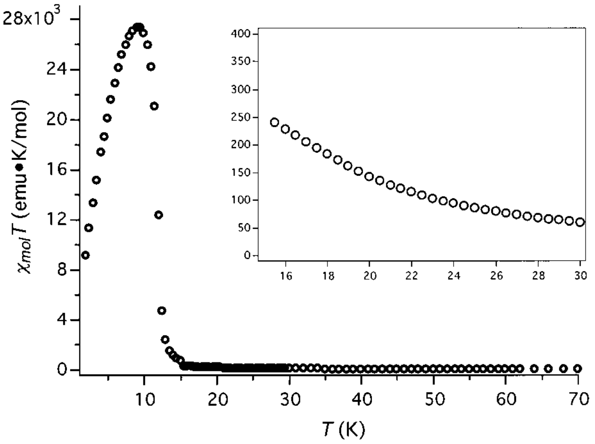

Figure 2. Temperature dependence of $\chi_{\mathrm{mol}}T$ values after irradiation of a 3:2 mixture (20 mM) of Cu(hfac)$_2$ and **2** in a frozen solution. The inset shows the enlarged view in the temperature range of 15−30 K.

(<40 Oe) depended on the concentration of the complex; FF occupied ca. 10, 25, and 70% of the M_{sat} values in 5, 10, and 20 mM concentrations, respectively. Weak hysteresis of M with respect to H was observed for FF; the coercive force and the remnant magnetization were ca. 2 Oe and 6.3×10^3 emu·Oe·mol^{-1}, repectively.[4,9] Furthermore, it is worth noting that the curvature of SF seems to be constant ($S = \sim 26-30$), suggesting that an assembly having single structure might be mainly produced in frozen solution.

Temperature dependence of the molar paramagnetic susceptibility, χ_{mol}[7] for 20 mM sample in the range of 2−70 K was measured at constant field of 0.002, 1, and 5 kOe below 15, 15−30, and above 30 K, respectively. $\chi_{\mathrm{mol}}T$ versus T plots are shown in Figure 2. The $\chi_{\mathrm{mol}}T$ value at 20 K amounted to 143 emu·Oe·mol^{-1} which was slightly greater than 116 emu·Oe·mol^{-1} for a tetramer of [{Cu(hfac)$_2$}$_3$·**2**$_2$]. As the temperature was decreased, the $\chi_{\mathrm{mol}}T$ value gradually increased in the range 20−12 K, then steeply increased, reached a maximum of 2.79×10^4 emu·Oe·mol^{-1} at 9 K,[10] and finally decreased. The observed gradual and steep developments of $\chi_{\mathrm{mol}}T$ value on cooling from 30 K may indicate the ferromagnetic interaction (30−15 K) between the carbene centers and copper(II) ions within the assemblies and the magnetic phase transition (<12 K), respectively.[11]

Single-molecule magnets[12] due to Mn(III, IV), Fe(II, III), Cr(III), and V(III) clusters are topics of recent interest. To know if FF showing the hysteretic properties might be a single-molecule magnet, ac magnetic susceptibility data for the same sample (20 mM) were collected in the temperature range 4.5−15 K with a 1 Oe ac field oscillating at the frequency of 1−750 Hz with a zero dc field. As shown in Figure 3, the temperature dependence of the in-phase and out-of-phase components, χ_M' and χ_M'', respectively, revealed relatively large round maxima and their peak-top temperature depended on the frequency of applied ac field; the temperature of the round maxima for χ_M' and χ_M'' (8.4−7.6 and 6.2−5.2 K, respectively) decreased, as the field alternation frequency decreased from 750 to1 Hz. The observed frequency dependence of χ_M' and χ_M'' corresponds better to a spin-glasslike response.[13]

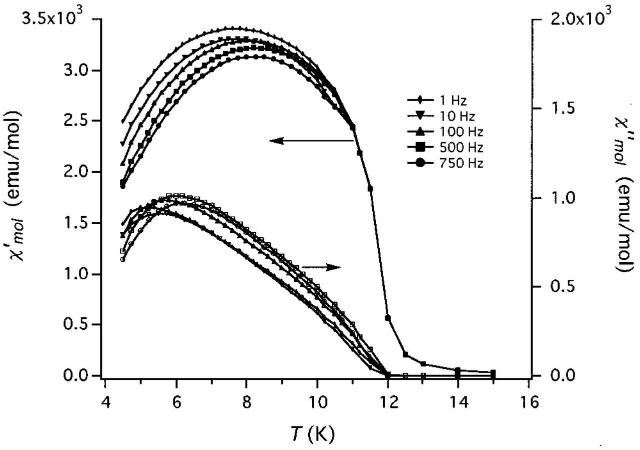

Figure 3. Temperature dependence of χ_M' and χ_M'' after irradiation of a 3:2 mixture (20 mM) of Cu(hfac)$_2$ and **2** in a frozen solution with a 1 Oe ac field oscillating (zero applied dc field) at the various frequencies. Arrows indicate the χ_M' and χ_M'' axes.

The magnetic behavior observed in the dc and ac magnetic susceptibility measurements was reproducible below 24 K. However, a decrease of the amount of FF in dc and the shift of peak-top to lower temperature in ac measurements were observed after annealing the sample in the temperature range 30−40 K. Both FF and, χ_M' and χ_M'', completely disappeared at temperatures greater than 50 K at which temperature the carbene centers start to decompose chemically. (The changes in the range 30−40 K are not clear at the present stage).

The magnetic behavior after photolysis of self-assemblies formed in the frozen solution strongly depends on the structure of photoresponsive magnetic coupler. For example, no FF was observed in a combination of Cu(hfac)$_2$ and 1-bromo-3,5-benzendiylbis(4-pyridyldiazomethane), which has a partial structure of **2**, under the condition similar to this work; they showed an increase of average S values (8−17) in proportion to the concentration in the range of 1.0−35 mM.[15] Although it is very difficult to reveal the structure of the self-assemblies formed in frozen solution, we took advantage of our hetero-spin system and could successfully construct complexes having spin-glasslike magnetic properties[16] by the simple procedure of mixing the two components in solutions and freezing them below 30 K followed by irradiation. The construction of the spin-glass reported here suggests a new approach to the single-molecule magnets by employing anisotropic metal ions in place of copper(II) ions.[17]

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(9) The value of the coercive force depends on the temperature; the value decreased on warming until 10 K.

(10) The maximum value corresponds to 995 units of 3:2 complex of Cu(hfac)$_2$ and **2**.

(11) The magnetization measurements by a sequence of zero-field cooled magnetization (ZFC), field-cooled magnetization (FCM), and remnant magnetization (RM) also suggested the magnetic phase transition below 10 K.

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(13) The value of $\Delta T_f/T_f(0)\Delta(\log w)$, where ΔT_f is the sift of the peak-temperature in χ'_M, log w is the logarithm of the applied frequency, and $T_f(0)$ is the position of the peak at zero frequency, obtained from the χ'_M vs T plot (Figure 3) is 0.04. According to Mydosh,[14] the value, 0.04, locates in a spin-glass region.

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(17) We thank a reviewer of this paper for reminding us of this possibility. Contrary to the suggested large zero-field splitting in the copper complexes with basic radical centers, the present Cu(II) complex having the doublet metal ion with the triplet carbene centers separated by a pyridine ring has smaller D value (unpublished results).