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Magnetic behaviors after irradiation of assemblies consisting of bis(hexafluoroacetylacetonato)copper(II) and tetrapyridyl-pentadiazo compound in frozen solution

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Abstract

Magnetic properties after irradiation of the mixture of $Cu(hfac)_2$ and tetrapyridine-pentadiazo compound **4** in $MTHF/CH_2Cl_2$ solutions by 1:2, 1:1, and 2:1 ratios were investigated by SQUID magneto/susceptometry. Field dependence of magnetization at 2 K after irradiation of the 1:2 mixture suggested the formation of high-spin complex, **4c**-$Cu(hfac)_2$-**4c**, with $S = 21/2$. In M vs. H plots for the 1:1 and 2:1 mixtures, hysteresis loops with coercive force, H_c ca. 1 and 2 Oe, respectively, were observed. In the a.c. magnetic susceptibility measurement of the 2:1 mixture under similar condition, in-phase and out-of-phase components (χ' and χ'', respectively) were observed below 18 K. The frequency dependence of peak-top temperature of χ' and χ'' suggested that its magnetic behavior was spin-glass like.

Keywords: Carbenes; Copper; Assembly; Spin-glass; Magnetic properties; Photolysis

1. Introduction

The various combinations of pyridines and metal ions have been used as the building block for the supramolecular architecture and have been reported forma one-, two-, and three-dimensional assemblies in solutions [1]. When pyridines possessing organic radical spins and paramagnetic 3d metal ions were employed, therefore, the hetero-high-spin assemblies [2–4] consisting of 3d metal ions and organic 2p spins were expected to be produced. Based on this idea together with our previous experiments [5] on the magnetic couplings between metal ions and organic spins through pyridine rings, photoresponsive magnetic couplers, diazodi(4-pyridyl)methane **1**, 1-bromo-3,5-benzenetriylbis(4-pyridyldiazomethane) **2**, 1,3,5-benzenetriyltris(4-pyridyldiazomethane) **3**, and diazobis{1-[3,5-benzenediylbis(4-pyridyldiazomethane)]}methane **4**, were prepared [6]. The 1:1 mixed ligand complexes of bis(hexafluoroacetylacetonato)copper(II), $Cu(hfac)_2$, coordinated with **1** and **2** formed ferromagnetic linear chains after irradiation [4]. Photoresponsive magnetic coupler **3** and **4** which have branched structures, are expected to form two- and/or three-dimensional assemblies after the complexation with $Cu(hfac)_2$. Actually, assembly consisting of the 3:2 mixture of $Cu(hfac)_2$ and PMC **3** in a frozen solution exhibited a spin-glass-like magnetic behavior below 12 K after irradiation [7]. In this work, tetrapyridyl-pentadiazo compound **4** having a highly branched structure was employed and the magnetic properties after irradiation of the mixture of $Cu(hfac)_2$ and **4** were investigated under the condition similar to the one for the $Cu(hfac)_2$-**3** assembly. Especially, by changing the ratios of $Cu(hfac)_2$ and **4** in the solutions, the relation between the structure formed in frozen solution and the magnetic property after irradiation was investigated. When they are mixed in a 1:2 ratio, the complex of **4**-$Cu(hfac)_2$-**4** will form in a frozen solution condition. By mixing in 1:1 and 2:1 ratios, on the other hand, assemblies having network structures are also expected to form under similar conditions.

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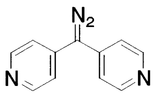

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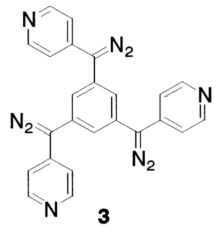

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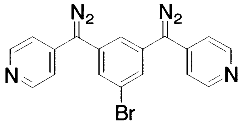

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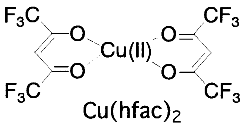
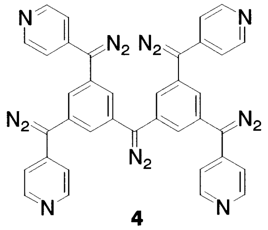


Cu(hfac)$_2$



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2. Experimental

2.1. General methods

Infrared spectra were recorded on a JASCO 420 FT-IR spectrometer. UV–Vis spectra were recorded on a JASCO V570 spectrometer. ^{1}H NMR spectra were measured on a JEOL 270 Fourier transform spectrometer using CDCl$_3$ as solvent and referenced to TMS. FAB mass spectra were recorded on a JEOL JMS-SX102 spectrometer. Melting points were obtained with a MEL-TEMP heating block and are uncorrected. Elemental analyses were performed in the Analytical Center of Faculty of Sciences in Kyushu University.

2.2. Magnetic measurements

D.c. and a.c. magnetic susceptibility measurements were performed on a Quantum Design MPMS-5S magneto/susceptometer. 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 [8]. The solutions (50 μl) of Cu(hfac)$_2$ in MTHF and PMC **4** in MTHF-CH$_2$Cl$_2$ (4:1) by 1:2, 1:1, and 2:1 molar ratio, respectively, were employed as the sample for the SQUID measurements. Magnetizations before and after irradiation (M_b and M_a, respectively) were collected at 2 and 5 K. The field dependence of the difference of magnetization ($M = M_\mathrm{a} - M_\mathrm{b}$) were analyzed by best-fitting of the Brillouin function $B(x)$ as given by Eq. (1).

$$M = M_\mathrm{a} - M_\mathrm{b} = \mu_\mathrm{B}\{(gSB(x) - g'B(x'))/2\} \qquad (1)$$

where $x = gS\mu_\mathrm{B}H/(k_\mathrm{B}T)$, $x' = g'\mu_\mathrm{B}H/(2k_\mathrm{B}T)$, and the other symbols have their usual meaning. In the experiments of the temperature dependence of χ_mol values for the 1:2 mixture, the values of $M_\mathrm{dia} = -6.0 \times 10^{-6}$ and -3.3×10^{-5} emu Oe in temperature range 2–15 and 15.5–20 K, respectively, were used. Those values were estimated by calculating from the M values at 0.2 and 1 kOe before irradiation at 2 K. In the zero-field cooled magnetization (ZFC) and field-cooled magnetization (FCM) experiments for 1:1 and 2:1 mixtures, d.c. field of 5 and 4.6 Oe were applied, respectively. Under the condition of applying low d.c. field, the diamagnetic term could be ignored. Photolysis of the sample was confirmed to take place quantitatively by taking the difference of absorptions [9] at 470 nm due to the diazo moieties before and after SQUID measurements. Saturation magnetization values (M_sat) obtained from the following experiments ranged 81.7–96.6% of the theoretical ones.

2.3. Materials

All solvents used in the reactions were purified by the reported methods. Tetrahydrofuran (THF) and ether were purified by distillation from sodium-benzophenone ketyl under a dry nitrogen atmosphere, just before use. All reactions were performed under an atmosphere of dry nitrogen unless otherwise specified.

2.3.1. *Bis(3,5-dibromophenyl)methyl tert-butyldimethylsilyl ether **4bp***

To the solution of bis(3,5-dibromophenyl)methyl alcohol [10] (5.0 g, 10 mmol) in 10 ml of DMF were added imidazole (2.8 g, 40 mmol) and *tert*-butyldimethylsilyl chloride (3.0 g, 20 mmol) at room temperature (r.t.). The reaction mixture was stirred at 40 °C for 5 h. After the neutralization with saturated sodium bicarbonate and the usual work-up, crude brown solid was chromatographed (Silica gel; eluent, *n*-hexane) to give protected bromide **4bp** as a white solid in a 89% yield (5.9 g, 8.9 mmol). M.p. 178 °C, Mass spectrum (Fab, *m*-nitrobenzyl alcohol matrix) *m*/*z* 615, 613 (M^+), ^{1}H NMR (CDCl$_3$, 270 MHz) δ 7.55 (dd, 2H, $J = 2.0$ and 1.7 Hz), 7.39 (d, 4H, $J = 1.7$ Hz), 5.54 (s, 1H), 0.91 (s, 9H), 0.02 (s, 6H). *Anal.* Calc. for C$_{19}$H$_{25}$SiBr$_4$: C, 37.16; H, 3.61, Found: C, 37.37; H, 3.68%.

2.3.2. *Bis[3,5-(4-pyridylhydroxymethyl)phenyl]methyl tert-butyldimethylsilyl ether, **4hp***

To the solution of **4bp** (3.0 g, 4.8 mmol) in 120 ml of anhydrous THF were added a 1.6 M solution of *n*-butyllithium (24 ml, 38 mmol) in *n* -hexane at −78 °C. After stirring for 4 h at −78 °C and then for 1 h at −30 °C, 4-formylpyridine (4.1 g, 38 mmol) was added dropwise. The reaction mixture was stirred for 1 h at −78 °C, for 1 h at −20 °C, and then for 0.5 h at 0 °C. After the usual work-up, resulting precipitates were collected by filtration. A crude mixture of tri- and tetraalcohol **4hp** were used for the oxidation without separation. A part of crude brown solid was chromatographed (Silica gel; eluent, $CHCl_3$:MeOH = 3:2) to give tetraalcohol **4hp** as a white solid. IR (KBr disc) ν_{OH} 3366 cm^{-1}, Mass spectrum (Fab, *m*-nitrobenzyl alcohol matrix) *m*/*z* 727 (M^+), ^{1}H NMR (DMSO-d_6, 270 MHz) δ 8.40 (d, 8H, $J = 5.1$ Hz), 7.36 (d, 8H, $J = 5.3$ Hz), 7.32 (m, 2H), 7.23 (d, 4H, $J = 6.4$ Hz), 5.71 (s, 4H), 3.34 (s, 1H), 3.30 (s, 4H), 0.72 (br 9H), −0.25 (br 6H).

2.3.3. *Bis[3,5-(4-pyridineoxomethyl)phenyl]methyl tert-butyldimethylsilyl ether* ***4kp***

To the solution of a crude mixture of alcohols (0.72 g, 1.0 mmol) in 20 ml of chloroform was added activated MnO_2 (1.60 g, 18.4 mmol). The suspension was stirred and refluxed for 4 h. After the usual work-up, yellow oil was obtained. The crude ketone was chromatographed (Silica gel; eluent, $CHCl_3$:MeOH = 97:3) to give tetraketone **4kp** (0.34 g, 0.48 mmol) and triketone (0.14 g, 0.28 mmol) as white solids. **4kp**; M.p. 69–71 °C, IR (KBr disc) ν_{CO} 1671 cm^{-1}, Mass spectrum (Fab, *m*-nitrobenzyl alcohol matrix) *m*/*z* 719 ($M^+ + 1$), ^{1}H NMR ($CDCl_3$, 270 MHz) δ 8.85 (d, $J = 6.0$ Hz, 8H), 8.10 (m, 6H), 7.57 (d, $J = 6.0$ Hz, 8H), 6.03 (s, 1H), 0.87 (s, 9H), −0.39 (s, 6H). *Anal.* Calc. for $C_{43}H_{38}N_4O_5Si$: C, 71.84; H, 5.33; N, 7.79. Found: C, 71.89; H, 5.33; N, 7.79%.

2.3.4. *Bis[3,5-(4-pyridyloxomethyl)phenyl]methyl alcohol,* ***4kh***

To the solution of tetraketone **4kp** (0.45 g, 0.63 mmol) in 30 ml of THF was added 1.0 M solution of tetrafluoroammoniumfluoride (6.3 ml, 6.3 mmol) in THF at r.t. The reaction mixture was stirred for 2 h. After the usual work-up, yellow oil was obtained. The crude alcohol was chromatographed (Silica gel; eluent, $CHCl_3$:MeOH = 19:1) to give alcohol **4kh** as a white solid in a 86% yield (0.33 g, 0.54 mmol) M.p. 105–107 °C, IR (KBr disc) 3443 (ν_{OH}), 1671 (ν_{CO}) cm^{-1}, Mass spectrum (Fab, *m*-nitrobenzyl alcohol matrix) *m*/*z* 606 ($M^+ + 1$), ^{1}H NMR ($CDCl_3$, 270 MHz) δ 8.83 (dd, 8H, $J = 1.7$ and 4.4 Hz), 8.15 (d, 4H, $J = 1.3$ Hz), 8.10 (t, 2H, $J = 1.6$ Hz), 7.57 (dd, 8H, $J = 1.6$ and 4.4 Hz), 6.17 (s, 1H). *Anal.* Calc. for $C_{37}H_{24}N_4O_5 \cdot 1.4CH_2Cl_2$: C, 62.61; H, 3.70; N, 7.57. Found: C, 62.73; H, 3.63; N, 7.54%.

2.3.5. *Bis{1-[3,5-benzendiylbis(4-pyridineoxomethyl)]}oxomethane,* ***4k***

To the solution of alcohol **4kh** (0.33 g, 0.54 mmol) in 15 ml of chloroform was added activated MnO_2 (0.32 g, 3.68 mmol). The suspension was stirred and refluxed for 3 h. After the usual work-up, crude ketones was obtained as yellow oil, which was chromatographed (Silica gel; eluent, $CHCl_3$:MeOH = 24:1) to give pentaketone **4k** (0.26 g, 0.43 mmol) as a white solid. M.p. 99–101 °C, IR (KBr disc) ν_{CO} 1674 cm^{-1}, Mass spectrum (Fab, *m*-nitrobenzyl alcohol matrix) *m*/*z* 603 (M^+), ^{1}H NMR ($CDCl_3$, 270 MHz) δ 8.88 (d, 8H, $J = 4.4$ Hz), 8.51 (m, 6H), 7.65 (dd, 8H, $J = 4.3$ and 1.7 Hz). *Anal.* Calc. for $C_{37}H_{22}N_4O_5 \cdot CH_2Cl_2$: C, 66.38; H, 3.52; N, 8.15. Found: C, 66.23; H, 3.73; N, 8.20%.

2.3.6. *Diazobis{1-[3,5-benzenediylbis(4-pyridyldiazomethane)]}methane,* ***4***

This was prepared by using **3k** in a manner similar to the procedure reported previously [3,4]. Diazo **4** was crystallized from ether–CH_2Cl_2 to give red plates [6]. M.p. (dec.) 105 °C, IR (KBr) $\nu_{C=N_2}$ 2048 cm^{-1}, UV–Vis (CH_2Cl_2; ε) 300 (114 100) and 495 (555) nm, Mass spectrum (Fab, *m*-nitrobenzyl alcohol matrix) *m*/*z* 663 (M^+), ^{1}H NMR ($CDCl_3$, 270 MHz) δ 8.50 (d, $J = 5.7$ Hz, 8H), 7.14 (br, 6H), 7.07 (d, $J = 5.7$ Hz, 8H). *Anal.* Calc. for $C_{37}H_{22}N_{14} \cdot 0.48CH_2Cl_2$: C, 64.02; H, 3.29; N, 27.89. Found: C, 64.29; H, 3.41; N, 27.59%.

3. Results and discussion

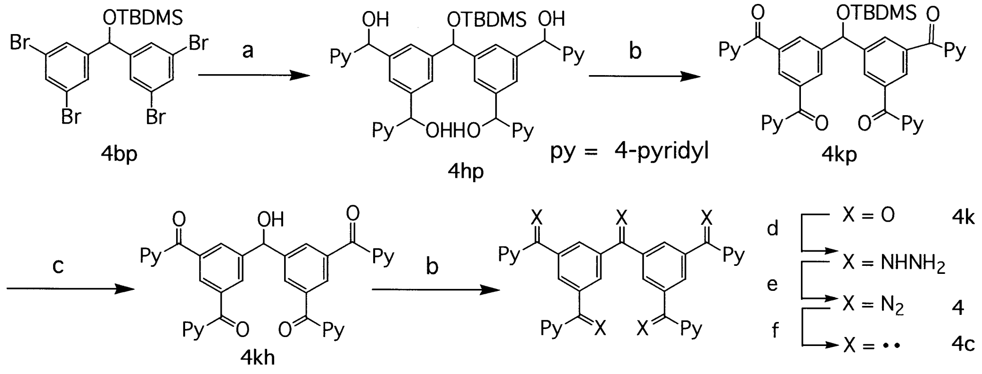
3.1. *Preparation of PMC* ***4***

Preparation of tetrapyridyl-pentadiazo **4** was summarized in Scheme 1. The tetralithiation of protected tetrabromo derivative **4bp** with *n*-butyllithium followed by the reaction with 4-formylpyridine gave a mixture of tri- and tetrapyridyl **4hp** compounds. As the solubility of a mixture was poor in organic solvent, a mixture was used for the further reaction without isolation. After the oxidation with activated manganese(IV) dioxide, they were separated by a silica gel column chromatography to tetraketone **4kp** and triketone derivatives. The deprotection of a silyl group and then the oxidation gave **4k** as white crystals. The carbonyl groups in **4k** were converted to the diazo groups by a standard procedure reported previously [3,4]. PMC **4** was recrystallized from ether–CH_2Cl_2 to afford red plates. The molecular structure of **4** revealed by X-ray analysis was reported previously [6].

Carbenes **4c** generated by photolysis of **4** was confirmed to be a ground state undecet ($S = 10/2$) by the magnetization (M) measurement under the conditions similar to the ones for the following experiments on the complex. Carbene centers in the complex of Cu(hfac)$_2$ with **4c** were also expected to interact ferromagnetically with copper(II) ions through the pyridine rings [4a,c,5b].

3.2. *Magnetic measurements after irradiation of the mixtures of Cu(hfac)$_2$ and PMC* ***4*** *in 1:2, 1:1, and 2:1 ratios*

The magnetic properties before and after irradiation of mixtures of Cu(hfac)$_2$ and PMC **4** in frozen solutions



a) *n*-BuLi, -78 °C, 4-formylpyridine, THF; b) MnO_2, $CHCl_3$, reflux;
c) TBAF, THF, r.t.; d) N_2H_4, $N_2H_4 \cdot HCl$, DMSO, 60 °C; e) MnO_2, $CHCl_3$, r.t.; f) *hν*

Scheme 1.

were studied by means of SQUID magneto/susceptometer. Photolysis of the samples, the 1:2, 1:1, and 2:1 mixtures of $Cu(hfac)_2$ and **4** in 0.75, 1.37, and 1.25 mM concentrations [11], respectively, were followed by the magnetization (M) measurement at 5 K in a constant field of 5 kOe. When the irradiation started, the M values gradually developed and leveled off after 2 h. The magnetization before and after irradiation (M_b and M_a, respectively) were also measured at 2 and 5 K in the field range of 0–50 kOe. The field dependences of the difference of M ($=M_a-M_b$) at 2 K between before and after irradiation were shown in Fig. 1 together with theoretical curves with $S=21/2$ and 10/2.

As shown in Fig. 1, the experimental data in M/M_s vs. H plot for the 1:2 mixture was closer to the theoretical curve with $S=21/2$ rather than the one with $S=10/2$; theoretical equation (Eq. (1)) fitted the experimental data to give $S=10.1$. The molar paramagnetic susceptibilities, χ_{mol}, for the 1:2 mixture after irradiation were measured in the range of 2–20 K at constant fields of 0.2 (< 15 K) and 1 kOe (> 15 K). Temperature dependence of χ_{mol} values after irradiation in the range 2–20 K was shown in Fig. 2. In the $\chi_{mol}T$ vs. T plot, the $\chi_{mol}T$ values gradually increased on cooling and reached a plateau below 3 K. Observed thermal behavior of $\chi_{mol}T$ indicates that the ferromagnetic interaction takes place in the complex. The value of $\chi_{mol}T$ at 2.5 K is 49.8 emu K mol^{-1}, which is close to the theoretical one (60.4) with $S=10.5$ for the 1:2 complex, $[Cu(hfac)_2 \cdot \mathbf{4}_2]$. These magnetic measurements suggest that the complex having a **4**-$Cu(hfac)_2$-**4** structure is mainly produced in a frozen solution.

On the other hand, the samples of the 1:1 and 2:1 mixtures exhibited interesting magnetic behaviors below 18 K. As shown in Fig. 1, the magnetization curves at 2 K for the samples of the 1:1 and 2:1 mixtures consist at least of two components, fast and slow saturating fractions (FF and SF, respectively) and FF occupied by 24 and 55% [12] of M_s values, respectively. Interest-

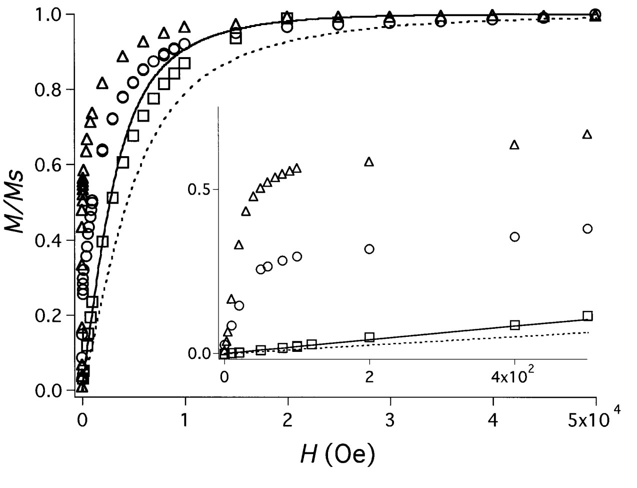


Fig. 1. Field dependence of the difference of M/M_s values at 2 K between before and after irradiation of 1:2 (□), 1:1 (○), and 2:1 (△) mixtures of $Cu(hfac)_2$ and **4** in frozen solutions. The low-field region (<0.5 kOe) is enlarged in the inset. Solid and dashed lines show theoretical curves with $S=21/2$ and 10/2, respectively.

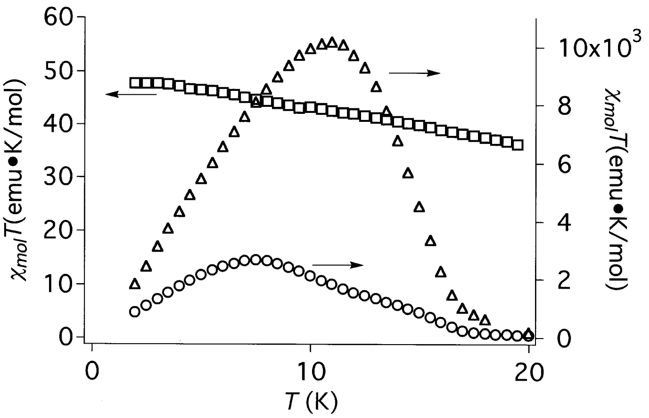


Fig. 2. Temperature dependence of $\chi_{mol}T$ values after irradiation of 1:2 (□), 1:1 (○), and 2:1 (△) mixtures of $Cu(hfac)_2$ and **4** in frozen solutions. Arrows indicate the axes.

ingly, FFs in both mixtures have weak hysteresis of M with respect to H below 10 K; the coercive force and the remnant magnetization (RM) at 2 K for the samples of the 1:1 and 2:1 mixtures were ca. 1 and 2 Oe, and 8.2×10^2 and 28.9×10^2 emu Oe mol^{-1}, respectively [13]. The temperature dependence of the M by a sequence of ZFC, FCM, and RM were also measured in the range of 2–20 K. As the temperature was decreased from 20 K, the M values of both of ZFC and FCM in M vs. T plots steeply increased at 18 K and started to deviate each other at ca. 7 K. The M values in RM on warming from 2 K gradually decreased and disappeared at ca. 10 K. The experimental data in FCM measurements were expressed in a fashion of $\chi_{\mathrm{mol}}T$ vs. T plot and were appended in Fig. 2. The temperature dependence of $\chi_{\mathrm{mol}}T$ values for the 1:1 and 2:1 mixtures showed the maxima of 0.27×10^4 and 1.02×10^4 emu K mol^{-1} at 7.5 and 11 K, respectively. Those values for the 1:1 and 2:1 mixtures correspond to 175 and 564 units of Cu(hfac)$_2$·**4** and {Cu(hfac)$_2$}$_2$·**4**, respectively.

In order to identify FF showing the hysteric properties, a.c. magnetic susceptibility data for the samples of the 2:1 mixture of Cu(hfac)$_2$ and **4** were collected in the temperature range 2–18 K with 3.9 Oe a.c. field oscillating at the frequency of 1–1000 Hz with a zero d.c. field. The temperature dependence of in-phase and out-of-phase components, χ'_{mol} and χ''_{mol}, respectively, are shown in Fig. 3. Both χ'_{mol} and χ''_{mol} components appeared below 18 K and had relatively round maxima, which were characteristic to a.c. measurements in frozen solution condition [14]. Their peak-top temperatures depended on the frequency of applied a.c. field; when the field alternation frequency decreased from 1000 to 1 Hz, the temperature of maxima for χ'_{mol} and χ''_{mol} (7.5–6.5 and 3.2–2.4 K, respectively) decreased. The value of $\Delta T_f/T_f(0)\Delta(\log w)$ obtained from the χ'_{mol} vs. T plot, where ΔT_f is the sift of the peak-temperature in χ'_{mol}, $\log w$ is the logarithm of the applied frequency, and $T_f(0)$ is the position of the peak at zero frequency, is 0.056. According to Mydosh [15], the value, 0.056, locates in a spin-glass region. The observed frequency dependence of χ'_{mol} and χ''_{mol} [16] seems more likely to suggest a spin-glass [17] rather than superparamagnet [18].

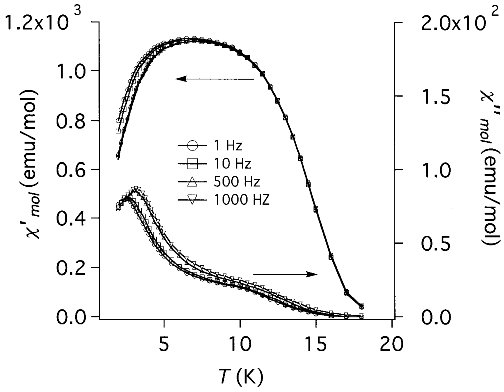


Fig. 3. Temperature dependence of χ'_{mol} and χ''_{mol} after irradiation of a 2:1 (△) mixture of Cu(hfac)$_2$ and **4** in a frozen solution with a 3.9 Oe a.c. field oscillating (zero applied d.c. field) at 1, 10, 500, and 1000 Hz. Arrows indicate the χ'_{mol} and χ''_{mol} axes.

The spin-glass like magnetic behaviors observed in the d.c. and a.c. magnetic susceptibility measurements were reproducible below 20 K. In the temperature range 21–30 K, the amount of FF decreased together with the shift of peak-top temperature to lower in a.c. measurements. After annealing at 30 K for 5 h, FF completely disappeared. However, the change of the M_s value was insignificant ($<7\%$), indicating that most of carbene survived under this temperature region. (The changes in the 20–30 K are not clear at the present stage). After leaving above 40 K at which the carbene centers start to decompose chemically, all magnetic behavior returned to the one before irradiation.

4. Conclusion

The magnetic behaviors after irradiation in frozen solutions strongly depend on the ratio of Cu(hfac)$_2$ and **4**. The magnetic measurement for the 1:2 mixture suggest to form the complex, **4c**-Cu(hfac)$_2$-**4c**, with $S = 10.5$. On the other hand, the 1:1 and 2:1 mixtures exhibited the spin-glass-like magnetic behaviors showing hysteresis properties below 10 K. The large difference between this work and the corresponding one for **3** [7] is that FF was observed in much smaller concentration (~ 10 times smaller); in 1.25 mM of the 3:2 mixture of Cu(hfac)$_2$ and **3**, FF was not detectable. The appearance of FF in the 1:1 mixture as well as the 2:1 mixture of Cu(hfac)$_2$ and **4** might suggest that the formation of FF was not strongly affected by the structure of assemblies. To increase the ratio of FF in frozen solutions, the improvement of the solubility of assemblies is in progress.

Acknowledgements

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