

Formation of Ferromagnetic Chains by Photolysis of 1:1 Complexes of Bis(hexafluoroacetylacetonato)copper(II) with Diazodi-4-pyridylmethane

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Abstract: Bis(hexafluoroacetylacetonato)copper(II) {Cu(hfac)₂} formed with diazodi-4-pyridylmethane yellow-green plates (**a**) and dark green bricks (**b**) in a 1:1 complex. X-ray crystal and molecular structure analysis of a single crystal of **a** revealed that the two pyridyl nitrogens of two different ligand molecules are coordinated with Cu(II) in a *trans* configuration to produce a one-dimensional chain. Complex **b** contains solvent molecules. The temperature dependence of molar magnetic susceptibility revealed that, while the complexes are dilute Cu(II) paramagnets before irradiation, they become ferromagnetic chains due to 3d spin of Cu(II) and 2p spins of di-4-pyridylcarbene generated by photolysis of the diazo group. The field dependence of magnetization revealed that the apparent spin quantum number of the ferromagnetic chains amounts to $S = \text{ca. } 33.6$ in complex **b**. A theoretical approach revealed that the ferromagnetic interaction between the neighboring Cu(II) and the carbene center along the chain amounts to $J/k_B = +66.8$ K. A 1:2 complex of Cu(hfac)₂ with diazophenyl-4-pyridylmethane (**2**) was prepared as a reference, and the photogenerated carbenes in the complex were found to interact with Cu(II) ions in a ferromagnetic fashion.

Introduction

Some free radicals having two or more ligating sites serve as bridging ligands for magnetic metal ions to form metal–radical complexes that have dinuclear or more extended structures of various dimensions and show interesting magnetic properties due to the ordered 2p and 3d heterospins. Semi-quinones,¹ nitronyl nitroxides,² di- and trinitroxides,³ and nitrogen bases carrying free radicals⁴ are typical examples. On the basis of this design strategy, a new bridging ligand, diazodi-4-pyridylmethane (**1**), was prepared.⁵ Compound **1** has two

kinds of functional groups, two pyridyl nitrogens and a diazo group. The former would make a polymeric chain structure by the ligation with metal ions, and the latter would be photolyzed to produce a carbene unit which plays a dual role of a triplet spin source and a magnetic coupling unit. Indeed, a 1:1 complex of bis(hexafluoroacetylacetonato)manganese(II), Mn(hfac)₂, with **1** formed a helical chain structure and became after photolysis a one-dimensional ferrimagnetic chain in which the interaction between the manganese ion and the generated carbene was *antiferromagnetic*.⁵ We report here the crystal structure and magnetic properties of the corresponding copper complex in which the interaction between the Cu(II) ion and the generated carbene proved to be *ferromagnetic* (Scheme 1).⁶ In order to evaluate the magnitude of this ferromagnetic interaction, we made two approaches: a theoretical analysis of the temperature dependence of the magnetic susceptibility data and an experimental evaluation of the magnetic interaction in a 1:2 complex of Cu(hfac)₂ with diazophenyl-4-pyridylmethane (**2**), a model complex corresponding to the 1.5 unit of the one-dimensional chain.

Results

Preparation of Ligands 1 and 2 and Their Copper(II) Complexes. Diazo compounds diazodi-4-pyridylmethane (**1**) and diazophenyl-4-pyridylmethane (**2**) were prepared by a standard method from the corresponding pyridyl ketones. The former was crystallized from dichloromethane–*n*-heptane to give red plates. Solutions of Cu(hfac)₂ in dichloromethane–methanol and **1** in dichloromethane were mixed in a 1:1 molar ratio at room temperature. The resulting yellow-green precipi-

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Table 1. Crystallographic Data and Experimental Parameters for **1**, Complex **a** of [Cu(hfac)₂·**1**], and [Cu(hfac)₂·**2**]

	1	[Cu(hfac) ₂ · 1] a	[Cu(hfac) ₂ · 2]
empirical formula	C ₁₁ H ₈ N ₄	C ₂₁ H ₁₀ N ₄ O ₄ F ₁₂ Cu	C ₃₄ H ₂₀ N ₆ O ₄ F ₁₂ Cu
formula wt	196.21	673.86	868.10
cryst color, habit	red, blocks	green, plates	brown, blocks
cryst dimens (mm)	0.50 × 0.40 × 0.25	0.20 × 0.050 × 0.40	0.30 × 0.20 × 0.20
cryst system	monoclinic	monoclinic	monoclinic
lattice params			
<i>a</i> (Å)	12.311(2)	8.031(2)	8.679(3)
<i>b</i> (Å)	11.178(3)	20.928(2)	10.055(2)
<i>c</i> (Å)	9.543(2)	15.095(2)	21.165(3)
β (°)	132.290(7)	94.29(2)	93.76(2)
<i>V</i> (Å ³)	971.6(3)	2529.9(7)	1842.9(7)
space group	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>Z</i> value	4	4	2
<i>D</i> _{calc} (g/cm ³)	1.341	1.769	1.564
no. of observations	642	1569	1841
no. of variables	87	434	300
residuals: <i>R</i> ; <i>R</i> _w	0.039; 0.073	0.052; 0.046	0.051; 0.041

Table 2. Selected Bond Lengths, Bond Angles, and Dihedral Angles for **1**, Complex **a** of [Cu(hfac)₂·**1**], and [Cu(hfac)₂·**2**]

	bond length (Å)		bond angle (deg)		dihedral angle (deg)	
1	Cu1—O1	2.008(3)	C3—C6—C3*	128.5(8)	C1C3C5—C1*C3*C5*	42.4(1) ^a
	Cu1—O2	2.281(3)				
	Cu1—N3	1.993(4)				
[Cu(hfac) ₂ · 1] a	Cu1—O1	2.031(8)	N1—Cu1—N4	178.5(1)	C1C3C5—C7C9C11	70.4(7) ^a
	Cu1—O2	2.232(7)				
	Cu1—O3	2.178(8)	Cu1—N4—C9	171.9(6)	N4C10C8—N1C2C4	59.0(2) ^b
	Cu1—O4	2.020(8)				
	Cu1—N1	2.012(8)	C3—C6—C9	126.4(1)		
	Cu1—N4	2.063(8)				
[Cu(hfac) ₂ · 2] 2	Cu1—O1	2.008(3)	N3—Cu1—N3*	180.000	C8C10C12—C2C4C6	58.93 ^a
	Cu1—O2	2.281(3)				
	Cu1—N3	1.993(4)	C4—C7—C10	126.8(4)	N3C9C11—N3*C9*C11*	0.00 ^b

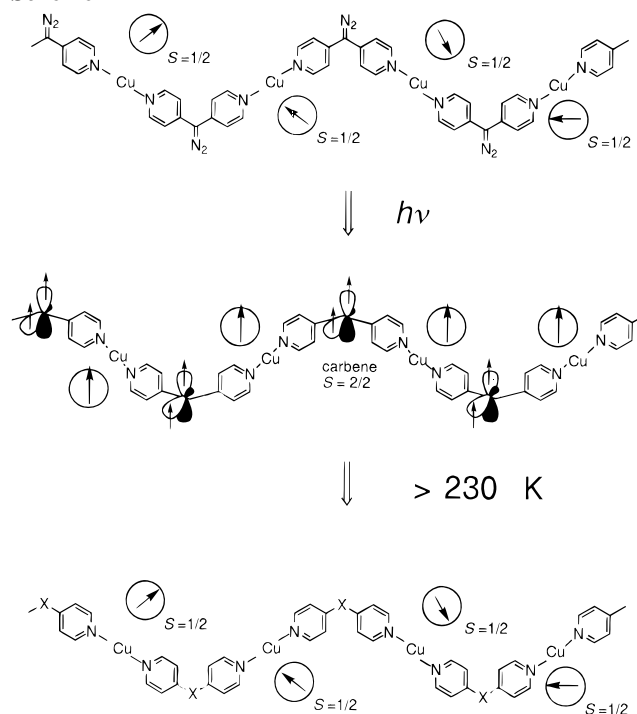
^a Dihedral angles between the two pyridyl rings through the diazo moiety. ^b Dihedral angles between the two pyridyl rings through the copper ion.

tates were recrystallized from methanol to give crystals **a** of [Cu(hfac)₂·**1**] as yellow-green plates. A similar reaction in dichloromethane–*n*-heptane followed by recrystallization of the precipitates from methanol–dichloromethane–benzene gave dark green bricks of complex **b**. A transparent crystal of **b** gradually became opaque when it was kept out of the solution. IR absorptions in a KBr disk of complexes **a** and **b** were superimposable to each other, and elemental analysis of the latter sample suggested that the initial crystals of **b** contained solvents of reaction and/or recrystallization.

A reference complex, [Cu(hfac)₂·**2**], was prepared in a manner similar to the procedure of [Cu(hfac)₂·**1**]**a** using two molar equivalents of **2** in place of one mole equivalent of **1**. Brown bricks of the 1:2 complex were obtained from dichloromethane–methanol–*n*-hexane.

X-ray Crystal and Molecular Structures. Single crystals of **1**, complex **a** of [Cu(hfac)₂·**1**], and [Cu(hfac)₂·**2**] were studied by using an X-ray diffractometer/data processor system. Pertinent crystallographic parameters and refinement data are collected in Table 1. Selected bond lengths, bond angles, and dihedral angles between two pyridine rings are summarized in Table 2. The molecular structure of **1** (Figure 1) has a *C*₂ symmetry axis through C6–N2–N3, a bond angle C3–C6–C3* of 128.5°, a torsion angle between the diazo moiety and pyridine plane of 23.6°, and a dihedral angle between the two pyridyl rings of 43.8°.

In the molecular and crystal structure of complex **a** of [Cu(hfac)₂·**1**] (Figure 2), the two pyridyl nitrogens of two different molecules of **1** are coordinated with a Cu(II) ion in a *trans* configuration to produce a one-dimensional chain structure parallel to the *ac* plane. Two trifluoromethyl groups in one of

Scheme 1

the two hfac ligands in Cu(hfac)₂ are disordered. The coordination geometry is a distorted octahedron; the bond distances are 2.031, 2.232, 2.178, and 2.020 Å for Cu–O and 2.012 and 2.063 Å for Cu–N, and the dihedral angles between the two pyridyl units through the diazomethyl unit and through the copper ion are 70.39° and 59.02°, respectively.

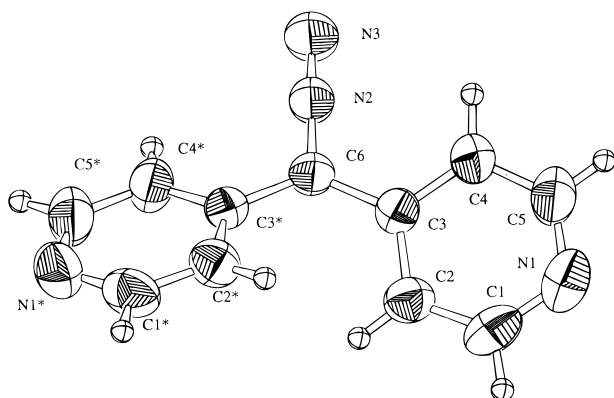


Figure 1. ORTEP drawing of the molecular structure for **1**.

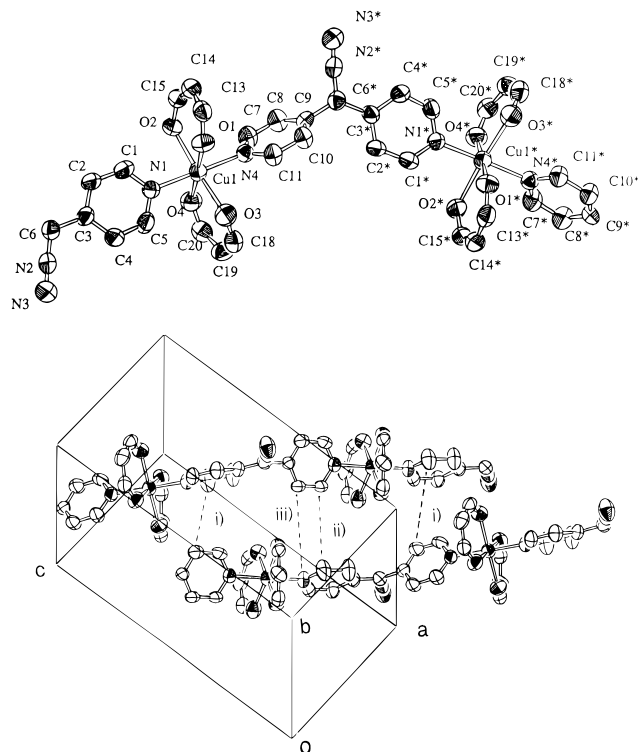


Figure 2. ORTEP drawing of (a, top) the molecular and (b, bottom) crystal structures of complex **a** of $[\text{Cu}(\text{hfac})_2 \cdot \mathbf{1}]$ in which the nearest two chains are represented. The trifluoromethyl groups are omitted for the sake of clarity. Broken lines indicate the distances between the chains: (i) 3.94 Å, (ii) 4.36 Å, and (iii) 4.84 Å.

The molecular structure of $[\text{Cu}(\text{hfac})_2 \cdot \mathbf{2}]$ showed that the two pyridyl nitrogens are ligated to the copper ion in a *trans* form (Figure 3a). The bond distances are 1.993 Å for Cu–N and 2.008 and 2.281 Å for Cu–O; the coordination geometry is a distorted octahedron. The dihedral angles between the two pyridyl units through the diazomethyl unit and through the copper ion are 58.9° and 0°, respectively. As shown in the crystal structure of Figure 3b, ligating molecules of **2** have neighboring molecules at a short distance of 3.86 Å, suggesting that the photogenerated carbenes would interact with each other intermolecularly.

Complex **a** has various distorted bond lengths and angles in the molecular structure, but the bond angle C3–C6–C9 of 126.4° (see Table 2) is close to the 126.8° bond angle in reference compound $[\text{Cu}(\text{hfac})_2 \cdot \mathbf{2}]$. The distance between the chains is relatively short, and one of the nearest contacts related to any magnetic interaction is 3.94 Å as indicated in Figure 3b.

Magnetic Measurements. Four or five pieces of fine crystals (ca. 0.5 mg) of complexes **a** and **b** of $[\text{Cu}(\text{hfac})_2 \cdot \mathbf{1}]$ and $[\text{Cu}$

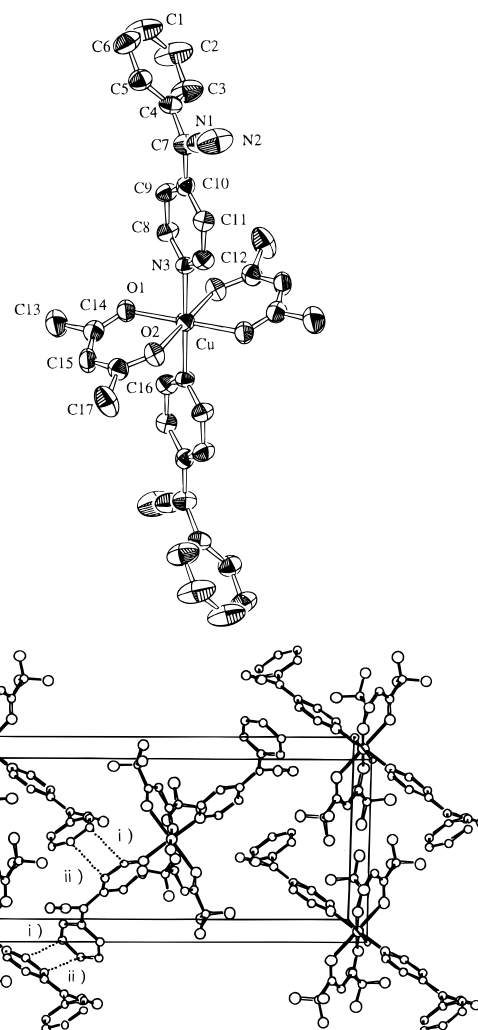


Figure 3. ORTEP drawing of (a) the molecular and (b) crystal structures of $[\text{Cu}(\text{hfac})_2 \cdot \mathbf{2}]$ in which the nearest molecules are represented. The trifluoromethyl groups are omitted for the sake of clarity. Broken lines indicate the distances between the atoms: (i) 3.94 Å, (ii) 4.36 Å, and (iii) 4.84 Å.

$(\text{hfac})_2 \cdot \mathbf{2}]$ were used for magnetic measurements on a SQUID susceptometer/magnetometer. Photolysis of the solid samples placed in a sample cell was carried out at 5–8 K with the second harmonic light ($\lambda = 532$ nm) from a Nd/YAG laser through an optical fiber. An IR absorption at 2072 cm^{-1} for complexes **a** and **b** of $[\text{Cu}(\text{hfac})_2 \cdot \mathbf{1}]$ disappeared completely after irradiation for 4 and 22 h, respectively. The corresponding absorption at 2064 cm^{-1} due to the diazo group of the complex $[\text{Cu}(\text{hfac})_2 \cdot \mathbf{2}]$ decreased to ca. 95% and 20% of the original after irradiation for 0.5 and 2.5 h, respectively.

Temperature dependencies of the molar magnetic susceptibility χ_{mol} (gram susceptibility times the formula weight of the complexes) for $[\text{Cu}(\text{hfac})_2 \cdot \mathbf{1}]$ in the range 2–300 K were measured at constant fields of 0.5 and 5 kOe below and above 70 K, respectively. For complex **b** of $[\text{Cu}(\text{hfac})_2 \cdot \mathbf{1}]$, not only the temperature dependence of χ_{mol} but also the field dependence of the magnetization (M) at 3 and 5 K in the field range 0–10 kOe were investigated alternately for a given sample. The measurements for $[\text{Cu}(\text{hfac})_2 \cdot \mathbf{2}]$ in the range 2–300 K were carried out at 0.5 and 5 kOe below and above 70 K, respectively. Out of two different runs after the irradiation for 0.5 and 2.5 h, only the former is shown in Figure 6. The changes in $\chi_{\text{mol}}T$ with the lapse of time are given in the inset.

The temperature dependencies of χ_{mol} are shown in Figures 4–6 in the form of $\chi_{\text{mol}}T$ vs T plots for complexes **a** and **b** of

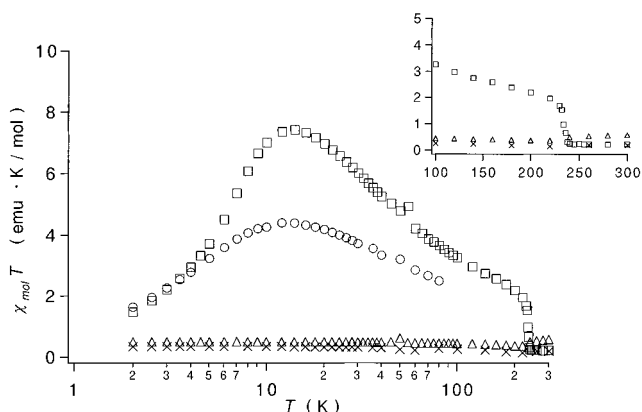


Figure 4. $\chi_{\text{mol}}T$ vs T for crystalline samples of complex **a** of $[\text{Cu}(\text{hfac})_2 \cdot \mathbf{1}]$ before (Δ) and after the irradiation for 2 h (\circ) and 4 h (\square), and then after being allowed to stand at 300 K for 15 min (\times). The inset shows the high-temperature region 150–300 K.

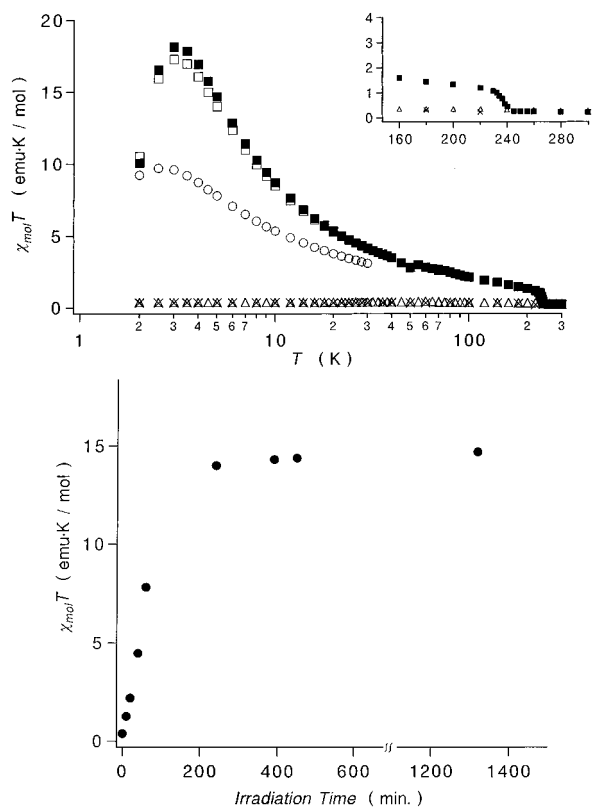


Figure 5. (a, top) $\chi_{\text{mol}}T$ vs T for crystalline samples of complex **b** of $[\text{Cu}(\text{hfac})_2 \cdot \mathbf{1}]$ before (Δ) and after the irradiation for 2 h (\circ), 4 h (\square), and 22 h (\blacksquare) and then after being allowed to stand at 300 K for 15 min (\times). The inset shows the high-temperature region 150–300 K. (b, bottom) Developments of the $\chi_{\text{mol}}T$ values at 5 K with irradiation time.

$[\text{Cu}(\text{hfac})_2 \cdot \mathbf{1}]$ and $[\text{Cu}(\text{hfac})_2 \cdot \mathbf{2}]$, respectively, before and after irradiation, and subsequent annealing at 300 K. Discontinuous changes in $\chi_{\text{mol}}T$ values observed at ca. 50 K are due to the adsorbed oxygen.

Discussion

(A) Magnetic Susceptibilities of Complexes a and b of $[\text{Cu}(\text{hfac})_2 \cdot \mathbf{1}]$. Before irradiation, $\chi_{\text{mol}}T$ values for the crystalline samples are nearly constant at 0.42 ± 0.08 and 0.38 ± 0.10 $\text{emu} \cdot \text{K} \cdot \text{mol}^{-1}$ for **a** and **b**, respectively, in the whole temperature range. These values are consistent with $\chi_{\text{mol}}T = 0.375$ $\text{emu} \cdot \text{K} \cdot \text{mol}^{-1}$ calculated for a dilute paramagnet of $S = 1/2$, indicating that the d electron spin of copper(II) ions is magnetically isolated.

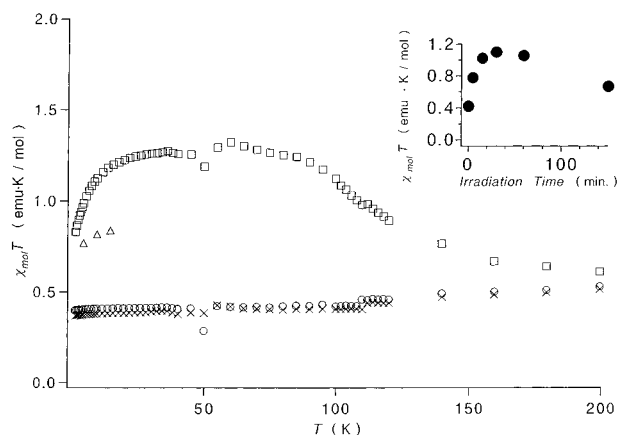


Figure 6. $\chi_{\text{mol}}T$ vs T for a crystalline samples of $[\text{Cu}(\text{hfac})_2 \cdot \mathbf{2}]$ before (\circ) and after the irradiation for 10 min (Δ) and 0.5 h (\square), and then after being allowed to stand at 300 K for 15 min (\times). The developments of the $\chi_{\text{mol}}T$ values at 5 K with irradiation time are given in the inset.

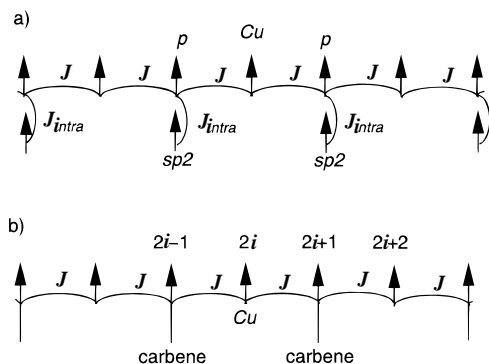
As the photolysis of the diazo group of the samples proceeded, the $\chi_{\text{mol}}T$ values started to grow and gradually leveled. For complex **b**, the development of the $\chi_{\text{mol}}T$ values at 5 K with irradiation time is demonstrated in Figure 5b. As the temperature was decreased, the $\chi_{\text{mol}}T$ values for complexes **a** and **b** after completion of the photolysis increased continuously, reached a maximum value of 7.43 and 18.2 $\text{emu} \cdot \text{K} \cdot \text{mol}^{-1}$ at 14 and 3.0 K, respectively, and started to decrease somewhat toward 2 K. The behavior is reversible up to 230 K, after which the $\chi_{\text{mol}}T$ values decreased sharply as shown in the inset of Figures 4 and 5a, respectively. In a consecutive measurement for the same sample left at 300 K, the $\chi_{\text{mol}}T$ values again traced the horizontal lines obtained before irradiation. The maximum $\chi_{\text{mol}}T$ values for **a** and **b** after irradiation far surpassed a value of 1.88 $\text{emu} \cdot \text{K} \cdot \text{mol}^{-1}$ for a $S = 3/2$ species which is expected for the ferromagnetically coupled set of the Cu(II) ion ($S = 1/2$) and triplet carbene ($S = 1$) unit. The increase of the $\chi_{\text{mol}}T$ values clearly demonstrates an increase in the correlation length of the ferromagnetic coupling along the one-dimensional heterospin chains with decreasing temperature.² The maximum $\chi_{\text{mol}}T$ values correspond to average correlation lengths of ca. 6 units at 14 K for **a** and ca. 15 units at 3 K for **b** along the chains. These correlation lengths should be taken as minimum estimates since they are not free from saturation at 0.5 kOe employed for the measurement (see Figure 9) and antiferromagnetic interchain interaction (see Figures 4 and 5a).

The difference in the temperature profile between complexes **a** and **b** after complete photolysis of the diazo units might be caused by a stronger interchain antiferromagnetic interaction in complex **a** than in **b**. The complex **a** before photolysis has a short distance between the chains by 3.97 Å as revealed by X-ray analysis. Although no information of a crystal structure for complex **b** is available at the present stage, complex **b** has presumably longer interchain distances by containing the solvent molecules in the crystal and/or by the *cis* configuration around the metal ions as observed in $[\text{Mn}(\text{II})(\text{hfac})_2 \cdot \mathbf{1}]$.⁵

Taking the temperature independence of $\chi_{\text{mol}}T$ above 240 K and in a consecutive measurement after leaving the sample at 300 K into account, we interpret the sharp change of the $\chi_{\text{mol}}T$ values at 240 K (inset of Figures 4 and 5a) as indicating a loss of the generated carbene centers by chemical reactions. Still the observed stability of the carbene centers is novel and most probably due to kinetic protection in the stiff crystal lattice of the metal complex as in the corresponding Mn(II) complex.^{5,6}

(B) Evaluation of the Ferromagnetic Interaction between the Neighboring Cu(II) and the Photogenerated Carbene

Scheme 2. Schematic Arrangement of the Spins within Alternating Chains in $[\text{Cu}(\text{hfac})_2 \cdot \{\text{di-4-pyridylcarbene}\}]$: (a) Cu–Carbene Sequence with p – sp^2 Spin Alignment at the Carbene Centers; (b) Effective Arrangement Assuming Strong Ferromagnetic p – sp^2 Coupling



Center. Two independent approaches, a theoretical simulation and the use of a closed model corresponding to the 1.5 unit of the polymeric complex, have been made for these purposes.

(B.1) Theoretical Approach to the Temperature Dependence of the Magnetic Susceptibility of Complex b of $[\text{Cu}(\text{hfac})_2 \cdot \mathbf{1}]$ after Photolysis. From a magnetic point of view, complex $[\text{Cu}(\text{hfac})_2 \cdot (\text{dipyridylcarbene})]$ consists of an alternating chain of copper(II) ($S = 1/2$) and carbenes ($S = 1/2 \times 2$) with two nearest neighbor exchange interactions, J between Cu(II) and carbene and J_{intra} between two unpaired electrons in the p and sp^2 -hybridized orbitals at the carbene center (Scheme 2a). Only the former interacts directly with $S = 1/2$ spin (d^9 orbitals) of the copper(II) ions through polarization of the p electrons on the pyridine ring. Furthermore, the spins at the carbene centers are strongly ferromagnetically coupled to each other by way of the one-center orthogonality of the orbitals. Thus, J_{intra} is safely assumed to be strongly ferromagnetic,⁷ and Scheme 2a reduces to Scheme 2b. The experimental behavior indicates that J is also ferromagnetic. Otherwise, the $\chi_{\text{mol}}T = f(T)$ curve should have exhibited a minimum, characteristic of a ferrimagnetic system.^{2,5}

As a result of strong ferromagnetic J_{intra} interaction, the carbene center may be described by an $S = 1$ ground state, thus coupled to adjacent copper(II) through J . At low temperature, the compound may thus be viewed as a collection of ferromagnetic chains of alternating $S = 1/2$ and $S = 1$ spins, as illustrated in Scheme 2, where J holds for an effective exchange interaction. This model is fully consistent with the high temperature value of $\chi_{\text{mol}}T$, which agrees with $1.38 \text{ emu} \cdot \text{K} \cdot \text{mol}^{-1}$ expected for isolated $S = 1/2$ and $S = 1$ spins.

Then, the effective spin Hamiltonian may be written as eq 1,

$$H = - \sum_i J S_{2i} (S_{2i-1} + S_{2i+1}) - \sum_i g \mu_B H (S_{2iz} + S_{2i+1z}) \quad (1)$$

where J refers to the interaction between the dipyridylcarbenes and Cu(II), described by the spin operators $S_{2i} = 1$ and $S_{2i+1} = 1/2$, respectively. Following the pioneering work of Bonner and Fisher for regular chains,⁸ calculations were performed for rings of increasing size, as a function of kT/J ($=1/x$). An overall g factor of 2.003 was used, which corresponds well to the

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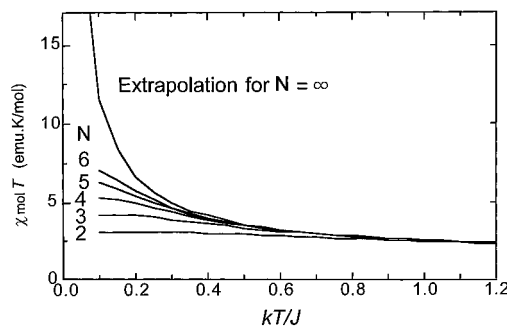


Figure 7. Calculation of $\chi_{\text{mol}}T$ versus kT/J for an alternating (1/2 to 1) ferromagnetic chain of N -dimeric spin units ($g = 2.003$), and extrapolation to infinity.

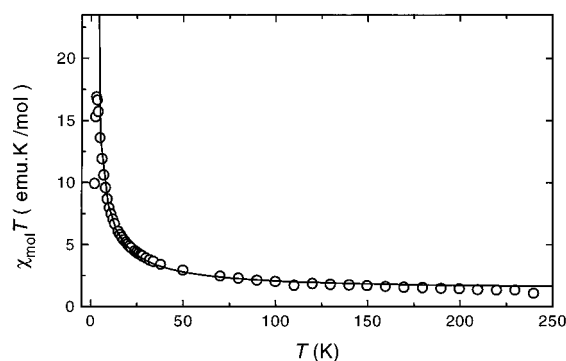


Figure 8. $\chi_{\text{mol}}T$ versus T plots for $[\text{Cu}(\text{hfac})_2 \cdot \{\text{di-4-pyridylcarbene}\}]$. The full line corresponds to the fit obtained by assuming the (1/2 to 1) alternating chain model (see text).

isotropic character of the spin carriers. Then, following the method of Drillon *et al.*,⁹ the behavior of the infinite chain was extrapolated from low temperature values of $\chi_{\text{mol}}T$ (kT/J) obtained for $N = 2, 3, 4, 5$, and 6 (1/2 to 1) spin units (Figure 7). The extrapolated curve was fitted with a polynomial fraction exhibiting conditions available at the limits. The best fit of the extrapolation corresponds to the following expression:

$$\chi_{\text{mol}}T = \frac{Ax^3 + Bx^2 + Cx + D}{Ex^2 + Fx + G} \quad (2)$$

with $A = 1.7701$, $B = 3.8283$, $C = 8.7057$, $D/G = 11/8$, $E = 1.9370$, and $F = 0.4145$.

Fitting to the experimental data has been performed by using the above expression for $T > 4$ K, giving $J/k_B = +66.8$ K, as the exchange interaction between the Cu(II) ions and the adjacent di-4-pyridylcarbene centers. The corresponding $\chi_{\text{mol}}T$ variation is compared with the experimental data in Figure 8.

(B.2) Reference Complex $[\text{Cu}(\text{hfac})_2 \cdot \mathbf{2}_2]$. An experimental estimate of the magnitude of the exchange coupling parameter in the $[\text{Cu}(\text{hfac})_2 \cdot \text{carbene}]$ complex was sought by employing a 1:2 reference complex, $[\text{Cu}(\text{hfac})_2 \cdot \mathbf{2}_2]$. This complex (Figure 3a) does not have an extended chain structure but corresponds to a model of a 1.5 unit of the one-dimensional infinite chain of $[\text{Cu}(\text{hfac})_2 \cdot \mathbf{1}]$.

Before irradiation, $\chi_{\text{mol}}T$ values of a fine crystalline sample of $[\text{Cu}(\text{hfac})_2 \cdot \mathbf{2}_2]$ were nearly constant at 2–300 K and observed values of 0.38 – $0.40 \text{ emu} \cdot \text{K} \cdot \text{mol}^{-1}$ in the whole temperature range are close to the theoretical spin-only value of $0.38 \text{ emu} \cdot \text{K} \cdot \text{mol}^{-1}$ expected for paramagnetic samples of $S = 1/2$. When irradiated ($\lambda = 532$ nm), the $\chi_{\text{mol}}T$ values developed with irradiation time; the values at 5 K increased for the first 0.5 h

(9) Coronado, E.; Drillon, M.; Georges, R. In *Research Frontiers in Magnetochemistry*; O'Connor, C. J., Ed.; World Scientific Publishing Co. Pte. Ltd.: Singapore, 1993; pp 27–66.

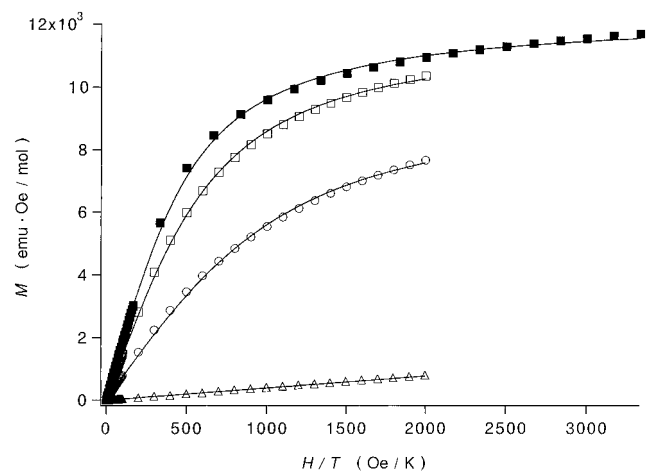


Figure 9. M vs HK for a crystalline sample of complex **b** of $[\text{Cu}(\text{hfac})_2 \cdot \mathbf{1}]$ at 5.0 K before (Δ) and after irradiation for 1 h (\circ) and 22 h (\square) and at 3.0 K after irradiation for 22 h (\blacksquare). Solid curves are theoretical ones calculated on the basis of the Brillouin function with $S = 1/2, 16.0, 26.0,$ and 33.6 .

and then decreased by further irradiation as indicated in the inset of Figure 6. As the temperature was decreased from 100 K in the dark after irradiation for 0.5 h, $\chi_{\text{mol}}T$ values gradually increased, reached a maximum of $1.3 \text{ emu} \cdot \text{K} \cdot \text{mol}^{-1}$ at 60 K, and then started to decrease at 30 K (Figure 6). The increase in the $\chi_{\text{mol}}T$ values from 100 to 60 K must most probably be interpreted in terms of the ferromagnetic interaction between the photogenerated carbenes and the copper ions.¹⁰ The decrease of $\chi_{\text{mol}}T$ values observed in the temperature range 30–2 K and by a prolonged irradiation (>0.5 h) is ascribed to intermolecular antiferromagnetic interaction between the photogenerated carbene centers. This antiferromagnetic interaction restricted us from estimating the magnitude of the ferromagnetic coupling by applying a theoretical linear three-spin model to the observed narrow $\chi_{\text{mol}}T$ versus T profile.

The temperature at which the carbene centers generated from $[\text{Cu}(\text{hfac})_2 \cdot \mathbf{2}_2]$ started to disappear was not as high as 240 K in the case of $[\text{Cu}(\text{hfac})_2 \cdot \mathbf{1}]$. Furthermore, it was dependent on the degree of photolysis: at ca. 200 K after 0.5 h and 120 K after 2.5 h irradiation. This phenomenon is probably related to the crystal structure of the complex in which diazo compound **2** has a neighboring molecule at a distance of 3.86 Å (Figure 3b).

(C) Magnetization of Complex b. Field dependencies of magnetization, M , for the same sample of complex **b** of $[\text{Cu}(\text{hfac})_2 \cdot \mathbf{1}]$ at 3 and 5 K before and after irradiation for 1 and 22 h, respectively, are reproduced in Figure 9. Before irradiation the M values were nearly proportional to the applied field in good agreement with a $S = 1/2$ paramagnet. When irradiation was started, apparent M values increased and their curvature in the M – H plot depended on the irradiation time, supporting the idea that the average S values increased with increasing amounts of the generated carbene centers by the photolysis. In order to estimate the average spins, the Brillouin function was applied to the magnetization data after completion of the photolysis at 3 K. The average spin quantum number S of the ferromagnetic chain under consideration is dependent on the correlation length, which in turn increases as the temperature is lowered and the applied field is increased. However, since the strength of the exchange coupling between the 3d spin of Cu(II) and the 2p spin of the carbene center in the present complex is estimated

to be as strong as $J/k_B = 67$ K (see section B.1), an estimate of the apparent S values at 3.0 K was made by applying the Brillouin function describing the magnetization of a paramagnetic sample consisting of an assembly of fixed spin S as a function of applied field strength and temperature. As in Figure 9, the best fits were obtained for the Brillouin function in which $S = 33.6 \pm 0.2$. These results correspond to the ferromagnetic coupling over ca. 23 units at 3 K along the chains.

Conclusion

The correlation length in the ferromagnetic chain obtained by irradiation of complex **b** of the dilute paramagnets $[\text{Cu}(\text{hfac})_2 \cdot \mathbf{1}]$ extends over ca. 23 units at 3 K. The ferromagnetic coupling between the Cu(II) ion and the coordinated di-4-pyridylcarbene is in contrast with the antiferromagnetic coupling in the corresponding Mn(II) complex⁵ and interpreted in terms of the orthogonality of the singly occupied $d_{x^2-y^2}$ atomic orbital of Cu(II) and the π -orbital on the pyridyl nitrogen which carries positive spin density with respect to the triplet carbene center.^{5,6}

The complexes described here constitute photochemically generated ferromagnetic chains (Scheme 1). Once a similar complex having higher dimensional network is constructed and spontaneous magnetization is obtained, the complex would serve as a photomagnetic device in which only the irradiated part becomes a magnet.¹¹

Experimental Section

General Methods. Infrared spectra were recorded on a Hitachi 270-30 spectrometer. Elemental analyses were performed in the Analytical Center of the Faculty of Science at Kyushu University.

X-ray Crystal and Molecular Structure Analysis. All the X-ray data were collected using Cu $K\alpha$ radiation on a Rigaku AFC5R four-circle diffractometer. Pertinent crystallographic parameters and refinement data are collected in Table 1. The structures of **1**, complex **a** of $[\text{Cu}(\text{hfac})_2 \cdot \mathbf{1}]$, and $[\text{Cu}(\text{hfac})_2 \cdot \mathbf{2}_2]$ were solved in $C2/c$ (No. 15), $P2_1/c$ (No. 14), and $P2_1/c$ (No. 14), respectively, by direct methods and refinement converged using the full-matrix least squares of the TEXAN Ver. 1.6 program (Molecular Structure Corp.). All non-hydrogen atoms were refined anisotropically; hydrogen atoms were included at standard positions (C–H 0.96 Å, C–C–H 109.5°, 120°, or 180°) and refined isotropically using a rigid model.

Magnetic Measurement before and after Photolysis. Magnetic susceptibilities were measured on a Quantum Design MPMS₂ SQUID susceptometer. Data were corrected for the magnetization of a sample holder, a quartz cell, and its lid used for diamagnetic contributions which were estimated from Pascal's constants.

The magnetic measurements of ca. 0.5 mg fine crystalline samples were performed before and after irradiation with a second harmonic light ($\lambda = 532$ nm) from Nd/YAG laser through an optical fiber at 5–8 K. It was later found not necessary to keep the temperature during irradiation in this range. Actually, the irradiation at 100 K gave a similar $\chi_{\text{mol}}T$ – T plot. The light intensity at the inside edge of the optical fiber was ca. 4–5 mW. The degree of the photolysis was estimated to be 100% and 80% for $[\text{Cu}(\text{hfac})_2 \cdot \mathbf{1}]$ and $[\text{Cu}(\text{hfac})_2 \cdot \mathbf{2}_2]$, respectively, as a whole by comparing the absorptivity at 2072 cm^{-1} for $[\text{Cu}(\text{hfac})_2 \cdot \mathbf{1}]$ and 2064 cm^{-1} for $[\text{Cu}(\text{hfac})_2 \cdot \mathbf{2}_2]$ due to the diazo groups of the complexes before and after the photolysis. The progress of the photolysis was found not to be even; the irradiated side of the crystalline samples suffered higher decomposition than the unirradiated side when inspected visually after the photolysis. Therefore, the production of the carbene species on the irradiated side of the crystals is judged to be higher than these figures. In the photolysis of the copper complexes, IR absorptions due to the diazo moiety disappeared completely after SQUID measurements. The temperature dependence of the magnetic

(10) In addition to this observation, analogous 1:2 copper complex ligated with 4-(*N*-*tert*-butyl-*N*-oxamino)pyridine showed ferromagnetic interaction of $J/k_B = 60.4 \pm 3.3$ K between the copper ion and the nitroxide radical.⁶

(11) Such an example consisting only of Prussian blue-type transition metal ions has recently been reported: Sato, O.; Iyoda, T.; Fujishima, A.; Hashimoto, K. *Science* **1996**, *272*, 704.

susceptibility χ_{mol} per formula unit was investigated under constant fields of 0.5 and 5 kOe below and above 70 K, respectively.

Materials. Solvents, diethyl ether, and toluene used for the reactions and spectral measurements were all distilled under high-purity N_2 after drying with sodium/benzophenone ketyl. Dichloromethane was distilled under high-purity N_2 after drying with calcium hydride. All reactions were stirred under an atmosphere of N_2 . Anhydrous magnesium sulfate was used as the drying agent. Solvents were removed on a rotary evaporator unless otherwise stated. $[\text{Cu}(\text{hfac})_2 \cdot 2\text{H}_2\text{O}]$ was prepared by the standard procedure. Diazodi-4-pyridylmethane (**1**) and 4-pyridylphenyldiazomethane (**2**) were prepared by the procedure reported previously.⁵

1:1 Complex a of $[\text{Cu}(\text{hfac})_2 \cdot \mathbf{1}]$. Solutions of $\text{Cu}(\text{hfac})_2$ in CH_2Cl_2 -MeOH and **1** in CH_2Cl_2 were mixed in a 1:1 molar ratio at room temperature, and the resulting yellow-green powder was collected. By crystallization from MeOH, complex **a** was obtained as yellow-green plates. Complex **a** of $[\text{Cu}(\text{hfac})_2 \cdot \mathbf{1}]$: IR (KBr) 2072 cm^{-1} . Anal. Calcd for $\text{C}_{21}\text{H}_{10}\text{N}_4\text{O}_4\text{F}_{12}\text{Cu}$: C, 37.43; H, 1.50; N, 8.35. Found: C, 37.53; H, 1.50; N, 8.31.

Complex b. A solution of 0.25 g of $[\text{Cu}(\text{hfac})_2 \cdot \text{H}_2\text{O}]$ in 50 mL of *n*-heptane was heated and reduced to 30 mL by distillation. The solution was cooled under a dry nitrogen atmosphere. To a still warm *n*-heptane solution was added a solution of 0.1 g of **1** in 30 mL of CH_2Cl_2 . A yellow-green powder precipitated immediately. Complex **b** $[\text{Cu}(\text{hfac})_2 \cdot \mathbf{1} \cdot (n\text{-heptane})_{0.2}]$: Anal. Calcd for $\text{C}_{21}\text{H}_{10}\text{N}_4\text{O}_4\text{F}_{12}\text{Cu}$

$(\text{C}_7\text{H}_{10})_{0.2}$: C, 38.79; H, 1.92; N, 8.08. Found: C, 38.69; H, 2.04; N, 7.99. This was crystallized from MeOH- CH_2Cl_2 -benzene to afford dark green bricks. $[\text{Cu}(\text{hfac})_2 \cdot \mathbf{1}]$: IR (KBr) 2072 cm^{-1} . After removal of the included solvents under reduced pressure, elemental analysis gave the following: Anal. Calcd for $\text{C}_{21}\text{H}_{10}\text{N}_4\text{O}_4\text{F}_{12}\text{Cu}$: C, 37.43; H, 1.50; N, 8.35. Found: C, 37.26; H, 1.50; N, 8.63.

Copper 1:2 Complex $[\text{Cu}(\text{hfac})_2 \cdot 2\mathbf{2}]$. This complex was prepared in a manner similar to the procedure of 1:1 complex **a** by using two molar equivalents of **2**. The complex was crystallized from CH_2Cl_2 -MeOH-*n*-hexane at room temperature to give orange bricks: IR (KBr) 2064 cm^{-1} . Anal. Calcd for $\text{C}_{34}\text{H}_{20}\text{N}_6\text{O}_4\text{F}_{12}\text{Cu}$: C, 47.04; H, 2.32; N, 9.68. Found: C, 47.05; H, 2.37; N, 9.69.

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Supporting Information Available: ORTEP drawing and details of the crystallographic analysis of **1**, $[\text{Cu}(\text{hfac})_2 \cdot 2\mathbf{2}]$, and complex **a** of $[\text{Cu}(\text{hfac})_2 \cdot \mathbf{1}]$ (45 pages). See any current masthead page for ordering and Internet access instructions.

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