Preparation of 5-trimethylsilyl-1,3-phenylenebis[diazo(4-pyridyl)methane] and magnetic properties of its 1:1 copper(II) complex after photolysis

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Photolysis of a paramagnetic 1:1 complex of copper(II) with 5-trimethylsilyl-1,3-phenylenebis[diazo(4-pyridyl)methane] produces a ferromagnetic chain consisting of an alternating array of 3d spins of Cu^{II} and 2p spins of the quintet dicarbenes.

Formation of metal complexes carrying free radical ligands has been proved to be a powerful design strategy for ordering heterospin systems consisting of 2p and 3d spins.[1,2] Based on this strategy, diazobis(4-pyridyl)methane **1** was designed and prepared.[3] The pyridine units are used to construct a polymeric chain structure by ligation with metal ions and the diazo moiety is photolyzed to produce the carbene unit which plays an important role as a triplet spin source as well as a magnetic coupling unit. 1 : 1 complexes of bis(hexafluoroacetylacetonato)-manganese(II) and -copper(II), Mn(hfac)$_2$ and Cu(hfac)$_2$, with **1** became one-dimensional ferri- and ferro-magnetic chains, respectively, upon photolysis.

To extend and improve these metal–carbene spin systems, we designed a 1,3-benzenediylbis[diazo(4-pyridyl)methane] derivative **2** carrying a bulky trimethylsilyl group at position 5 to attenuate the interchain antiferromagnetic interaction and also coupled this photoresponsive ligand with Cu(hfac)$_2$ to give [Cu(hfac)$_2$·**2**] in which the generated quintet carbenes are expected to interact with the copper ions ferromagnetically, as illustrated in Scheme 1.

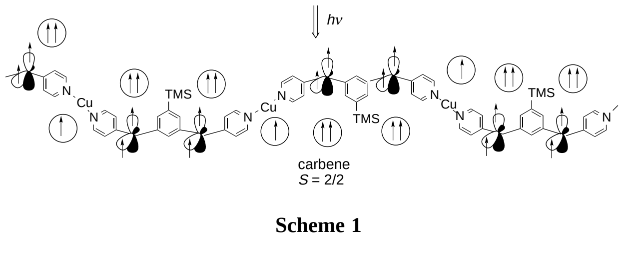
1,3-Dibromo-5-trimethylsilylbenzene was lithiated with Bu^{t}Li in anhydrous diethyl ether and reacted with 4-cyanopyridine, followed by hydrolysis with aq. H_2SO_4. The dipyridyl diketone thus obtained was converted to diazo compound **2** by a usual procedure[3] *via* the corresponding dihydrazone. Compound **2** was crystallized from diethyl ether as red bricks [mp = 109 °C (decomp.)] and its molecular structure was investigated by X-ray analysis.† The molecular structure of **2** has a mirror plane passing through C(8) and C(10) in the benzene ring and the pyridyl groups are directed to the opposite side of the trimethylsilyl group. The dihedral angle between the pyridyl groups and the benzene ring is 44.86° (Fig. 1).

In the EPR spectrum after photolysis of **2** in frozen 2-methyltetrahydrofuran, signals characteristic of quintet dicarbene[4] with a zero-field splitting parameter D in the range 0.07–0.13 cm^{-1} were observed in addition to weak signals due to a monocarbene. The intensities of the quintet signals decreased according to Curie behaviour in the temperature range 10–74 K, suggesting that the quintet is a ground state. By mixing a solution of Cu(hfac)$_2$ in MeOH and **2** in MeOH–CH_2Cl_2, the 1 : 1 complex [Cu(hfac)$_2$·**2**] was obtained as brown microcrystals. Although no structural information‡ for the complex was obtained, it is reasonable to assume an infinite chain structure since in the two pyridyl nitrogens are ligated to two different metal ions to produce chain structures in the corresponding manganese(II) complex, [Mn(hfac)$_2$·**2**]† (Fig. 2), prepared under similar conditions and the analogous [Cu(hfac)$_2$·**1**].[5]

A microcrystalline sample (*ca.* 0.5 mg) of [Cu(hfac)$_2$·**2**] was used for magnetic measurements on a SQUID susceptometer. The sample placed inside the sample compartment of the susceptometer was irradiated at 5–7 K with second harmonic light (λ = 532 nm) from a Nd/YAG laser through an optical fiber.[5] After iradiation for 10 h, followed by SQUID measurements, IR absorptions of the sample at 2068 cm^{-1} due to the diazo groups of [Cu(hfac)$_2$·**2**] disappeared completely.

The temperature dependences of the molar magnetic susceptibility χ_{mol} per formula unit of [Cu(hfac)$_2$·**2**] are shown in Fig. 3 in the form of $\chi_{\mathrm{mol}}T$ *vs.* T plots before and after irradiation, and subsequent annealing at 300 K. Before irradiation, $\chi_{\mathrm{mol}}T$ values are nearly constant at 0.55 ± 0.03 emu K mol^{-1} in the temperature range 2–200 K. These values are close to that ($\chi_{\mathrm{mol}}T$ = 0.38 emu K mol^{-1}) calculated for a dilute $S = \frac{1}{2}$ paramagnet, indicating that the d electrons of Cu^{II} are magnetically isolated.

The $\chi_{\mathrm{mol}}T$ values after the photolysis of [Cu(hfac)$_2$·**2**] for 10 h increased continuously with decrease in temperature from 100 K, reached a maximum value of 23.4 emu K mol^{-1} at 5.0 K, and decreased below 5 K. This behavior is reversible up to 100 K after which the $\chi_{\mathrm{mol}}T$ values decreased at different rates as observed in Fig. 3. In a consecutive measurement for the same sample left at 300 K, $\chi_{\mathrm{mol}}T$ showed the behavior prior to



Scheme 1

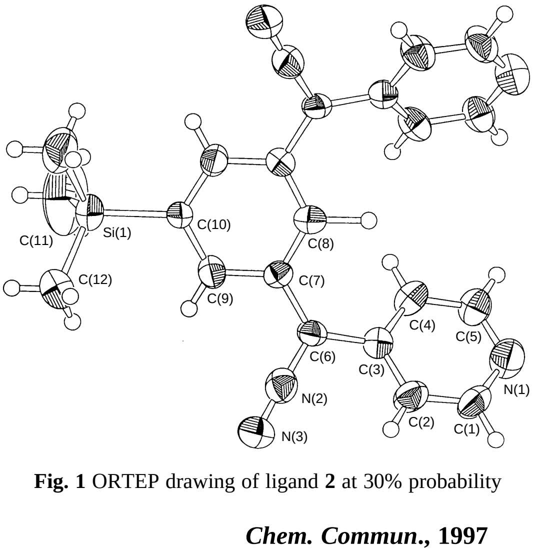


Fig. 1 ORTEP drawing of ligand **2** at 30% probability

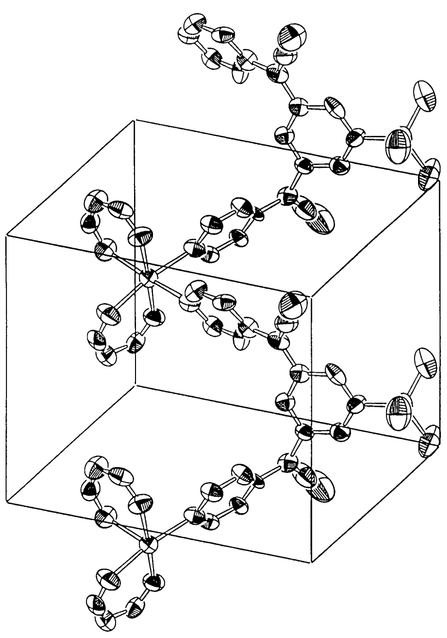


Fig. 2 ORTEP drawing of [Mn(hfac)$_2$·**2**] at 30% probability

irradiation. A maximum value of 23.4 emu K mol^{-1} after irradiation for 10 h far surpasses the theoretical value of 4.37 emu K mol^{-1} for an S = 5/2 species expected for a single unit produced by ferromagnetic interaction between Cu^{II} (S = 1/2) and a quintet carbene (S = 4/2) in the complex. The increase of $\chi_{mol}T$ as the temperature was decreased from 100 to 5 K clearly demonstrates an increase of the correlation length of the ferromagnetic coupling along the one-dimensional heterospin chain with decreasing temperature. The decrease of $\chi_{mol}T$ below 5 K might be caused by an interchain antiferromagnetic interaction.

Taking into account the temperature independent $\chi_{mol}T$ values above 100 K and those in a consecutive measurement after annealing the sample at 300 K, we interpret the irreversible change of $\chi_{mol}T$ at 100 K as indicating a chemical loss of the generated carbene centers.

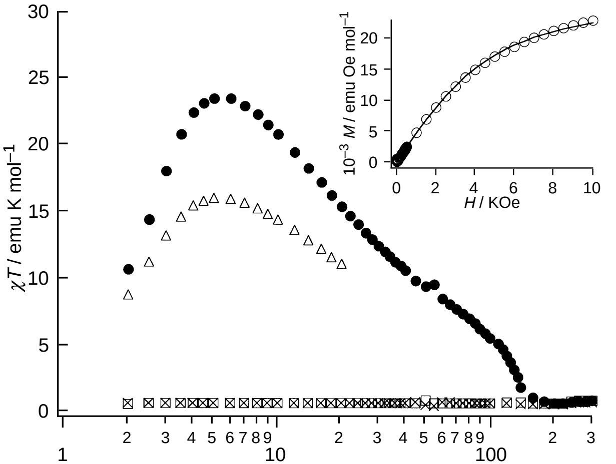


Fig. 3 Temperature dependences of $\chi_{mol}T$ per formula [Cu(hfac)$_2$·**2**] for a powder sample before (□) and after irradiation for 2 (△) and 10 h (●), and then annealing at 300 K for 1 h (×). The field dependence of magnetization M for [Cu(hfac)$_2$·**2**] at 5 K is given in the inset. The solid curve is the theoretical fit § (S = 17.25 ± 0.01).

In order to estimate the ferromagnetic correlation length, the field dependences of magnetization M for the same sample of [Cu(hfac)$_2$·**2**] after irradiation for 10 h at 5 K were investigated. A theoretical curve represented by a Brillouin function§ was fitted to the experimental data by a least-squares method to give S = 17.25 ± 0.06, as indicated by the solid curve in the inset of Fig. 3. This value corresponds to a ferromagnetic coupling of *ca.* seven units at 5 K along the chains. This estimate of the correlation length obtained from the M–H plots is consistent with that (*ca.* 7 units)¶ from the maximum value at 5 K in the $\chi_{mol}T$–T plot.

Although it can not be stated at the present stage if the bulkiness of the trimethylsilyl group was effective in weakening the antiferromagnetic interchain interaction, [Cu(hfac)$_2$·**2**] did show a higher maximum $\chi_{mol}T$ compared to the corresponding unsubstituted copper complex.[6] It is concluded that the photochemical generation of two triplet carbene centers coupled ferromagnetically to each other through the *m*-phenylene ring and consequent magnetic coupling of these 2p spins with 3d spins of Cu^{II} through the pyridine rings established a one-dimensional ferromagnetic chain (Scheme 1).

Footnotes

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[†] *Crystal data*: **2**: C$_{21}$H$_{20}$N$_6$Si, M = 384.51, orthorhombic, space group *Pnma* (no. 62), a = 19.205(3), b = 17.308(3), c = 6.137(3) Å, U = 2039(1) Å^3, T = 296 K, Z = 4, D_c = 1.252 g cm^{-3}, μ(Cu-Kα) = 11.59 cm^{-1}, 1845 total (1800 independent) reflections, R = 0.062 and R_w = 0.044 for 595 reflections with $I > 3\sigma(I)$. [Mn(hfac)$_2$·**2**]: C$_{31}$H$_{22}$O$_4$F$_{12}$MnN$_6$Si, M = 853.56, triclinic, space group $P\bar{1}$ (no. 2), a = 13.069(1), b = 13.284(2), c = 10.917(2) Å, α = 91.07(1), β = 90.50(1), γ = 81.975(9)°, U = 1876.4(4) Å^3, T = 296 K, Z = 2, D_c = 1.511 g cm^{-3}, μ(Cu-Kα) = 41.19 cm^{-1}, 4393 total (4110 independent) reflections, R = 0.060 and R_w = 0.048 for 497 reflections with $I > 3\sigma(I)$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/503.

[‡] In solution diazo moieties of the complex was relatively unstable at room temperature and growth of a single crystal for X-ray analysis was prevented by this instability.

[§] $M = NgS\mu_B B(x)$ where $B(x)$ is a Brillouin function, where $x = gS\mu_B H/(k_B T)$, and the other symbols have their usual meanings.

[¶] The correlation length (n = number of units) was estimated by the following equation: $n\chi_{mol}T = 0.125\,g^2 nS\,(nS + 1)$, where $\chi_{mol}T$ = 23.4, g = 2, and S = 5/2.

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