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# Ferromagnetic Coordination Polymer Composed of Heterocyclic Thiazyl Radical, 1,3,5-Trithia-2,4,6-triazapentalenyl (TTTA), and Bis(hexafluoroacetylacetonato)copper(II) (Cu(hfac)$_2$)

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The adducts of metal complexes and organic free radicals have been extensively studied.[1−4] The interactions between the metal ions and the organic radicals are fundamentally important in magnetochemistry, materials science, biochemistry, etc. The organic radicals are also attracting interest as a building block of supramolecular magnets.[5]

The thiazyl free radicals possess chemical stability and strong intermolecular interactions. Various interesting properties have been revealed so far.[6−10] Recently we reported that 1,3,5-trithia-2,4,6-triazapentalenyl (abbreviated as TTTA) showed a unique first-order phase transition between a paramagnetic high-temperature phase and a diamagnetic low-temperature phase, with a large thermal hysteresis loop in the temperature range 230−305 K.[11] In this work we developed a new aspect of the thiazyl radicals; we elucidated the ability of TTTA as a ligand to form polymeric coordination complexes. In general, the nitrogen atoms in the thiazyl radicals bear negative polarized charges and basicities. It is expected that the nitrogen atoms in TTTA coordinate to metal ions, resulting in network structures. We report the crystal structure and the magnetic properties of the 1:1 complex of TTTA and bis(hexafluoroacetylacetonato)copper(II) (abbreviated as Cu(hfac)$_2$).

TTTA was prepared by a modification of the literature method.[12] Cu(hfac)$_2$ was purchased from the Tokyo Kasei Co. Ltd. and was used without purification. The 1:1 complex TTTA·Cu(hfac)$_2$ was obtained by the reaction of stoichiometric amounts of the components in hot heptane solution under nitrogen atmosphere. The deep blue plate-like crystals were obtained at −30 °C.

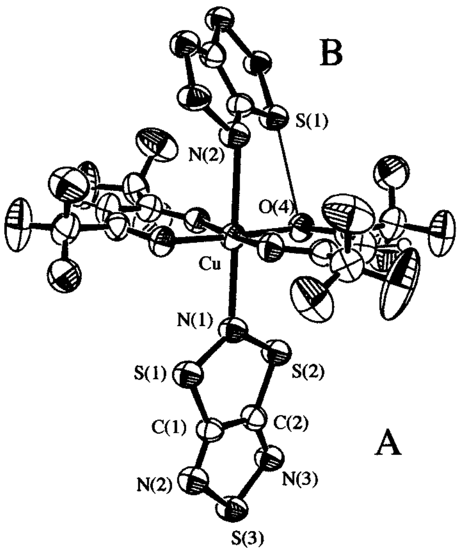

**Figure 1.** ORTEP drawing of TTTA·Cu(hfac)$_2$. Thermal ellipsoids are drawn at the 50% probability level. Selected interatomic distances (Å): Cu−O(1) 1.949(4), Cu−O(2) 1.974(4), Cu−O(3) 1.973(4), Cu−O(4) 1.951(4), Cu−N(1) 2.342(4), Cu−N(2) 2.479(4), S(1)−O(4) 3.208(4).

The complex TTTA·Cu(hfac)$_2$ crystallizes in the monoclinic $P2_1$ space group, in which one unit of TTTA·Cu(hfac)$_2$ is crystallographically independent.[13] Figure 1 depicts the geometry around the Cu(II) ion in this compound, where Cu(hfac)$_2$ and one of the TTTA molecules labeled A form the independent unit. The other TTTA labeled B is obtained by the symmetry operation ($-x + 1$, $y + 0.5$, $-z + 1$) from TTTA$^A$. The metal ion is coordinated in a tetragonally distorted octahedron to six atoms, four of which are the oxygen atoms of the two hfac ligands. They occupy the coplanar equatorial coordination sites at bonding distances of 1.949(4)−1.974(4) Å. The axial coordination sites are occupied by TTTA, where the distances of Cu−N(1)$^A$ and Cu−N(2)$^B$ are 2.342(4) and 2.479(4) Å, respectively. The former is shorter than the latter by more than 0.1 Å. The atom N(1) belongs to the dithiazolyl ring on which the singly occupied molecular orbital (SOMO) is rather localized,[11] while N(2) is on the thiadiazole ring. The magnetic interaction between Cu(II)−TTTA$^A$ would be much stronger than that between Cu(II)−TTTA$^B$. The remaining nitrogen atom, N(3), on TTTA does not coordinate to the Cu(II) ions. The molecular plane of TTTA$^A$ is closely orthogonal to the plane defined by the four hfac oxygen atoms: there is an orthogonal relation between the SOMO of TTTA$^A$ and the magnetic $d_{x^2-y^2}$ orbital on the Cu(hfac)$_2$ molecular plane. The central Cu(hfac)$_2$ probably has a ferromagnetic coupling with TTTA$^A$. On the other hand, the molecular plane of TTTA$^B$ is significantly tilting to the plane of Cu(hfac)$_2$. There is a short distance of 3.208(4) Å between S(1) on TTTA$^B$ and O(4) in the hfac ligand, probably caused by an electrostatic interaction, reflecting the strong electric polarization in TTTA. This contact suggests an overlap between the magnetic orbitals of TTTA$^B$ and Cu(hfac)$_2$, which results in an antiferromagnetic interaction.

Figure 2 shows a view of the crystal structure for TTTA·Cu(hfac)$_2$, in which CF$_3$ groups of Cu(hfac)$_2$ are omitted. TTTA bridges the distance between the Cu(II) ions, resulting in an

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(13) Crystal data: $C_{12}H_2F_{12}N_3O_4S_3Cu$, $M = 639.87$, monoclinic, $a = 6.937(4)$ Å, $b = 14.252(6)$ Å, $c = 10.699(7)$ Å, $\beta = 103.843(2)°$, $Z = 2$, $U = 1027.05(10)$ Å$^3$, $T = 293$ K, space group $P2_1$ (no. 4), $\mu = 1.505$ mm$^{-1}$, 4519 reflections measured, 4511 unique ($R_{int} = 0.046$) which were used in all calculations. The final $wR(F^2)$ was 0.038 (all data).

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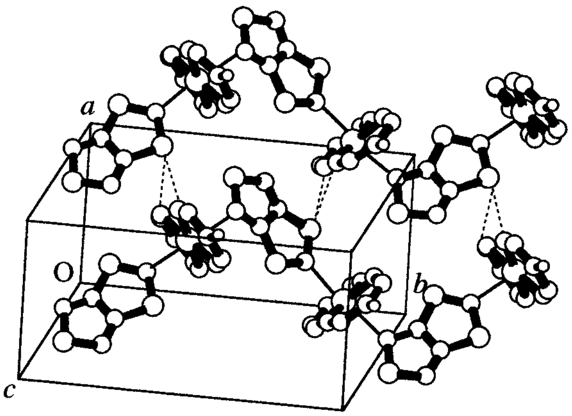

**Figure 2.** A view of the crystal structure for TTTA·Cu(hfac)$_2$. The CF$_3$ groups of Cu(hfac)$_2$ are omitted for the sake of clarity. The interchain contacts are shown by the broken lines.

infinite zigzag chain along the *b* axis. In the interchain arrangement, there are two short contacts between the sulfur atom on the dithiazolyl ring and the oxygen atoms of Cu(hfac)$_2$ (3.072(4) and 3.271(4) Å), as shown by the broken lines in Figure 2. While Rawson et al. reported the mono-, di-, and trimetallic coordination compounds of 1,2,3,5-dithiadiazolyl radicals,[4] TTTA·Cu(hfac)$_2$ is the first coordination polymer made of the thiazyl radicals. Caneschi et al. discovered a 1D coordination polymer of Cu(hfac)$_2$ and a nitronylnitroxide in which the organic radical acted as a bidentate ligand.[14] This was a breakthrough to the chemistry of the adducts of the metal complexes with various nitronylnitroxides[1] and polynitroxyl radicals.[2] Recently Hicks et al. reported novel coordination compounds of a verdazyl radical.[15] The polycyclic thiazyl radicals, such as TTTA, possess similar chemical capability.

The magnetic measurements on TTTA·Cu(hfac)$_2$ were performed on a Quantum Design MPMS-XL SQUID susceptometer. The diamagnetic correction was performed, using a diamagnetic susceptibility evaluated on the assumption that the paramagnetic component $\chi_p$ followed the Curie law at high temperatures. Figure 3 depicts the temperature dependence of $\chi_pT$ for TTTA·Cu(hfac)$_2$ in the range 1.8−300 K. We adopt TTTA·Cu(hfac)$_2$ as the molar unit. The value of $\chi_pT$ at 300 K is 0.793 emu K mol$^{-1}$ that is close to the ideal value (0.812) for noninteracting two $S = {}^1/_2$ spins on $g = 2.153$ (Cu(hfac)$_2$)[16] and 2.006 (TTTA).[12] As the temperature is decreased from 300 to 30 K, the value of $\chi_pT$ shows a gradual increase, indicating a ferromagnetic coupling. After passing through a maximum of 0.848 emu K mol$^{-1}$ at 30 K, $\chi_pT$ shows an abrupt decrease, suggesting a weak antiferromagnetic coupling between the ferromagnetic units. It is reasonable to ascribe the ferromagnetic coupling to the coordination bond between Cu(hfac)$_2$ and TTTA$^{\mathrm{A}}$, and to do the antiferromagnetic coupling to the interaction between Cu(hfac)$_2$ and TTTA$^{\mathrm{B}}$ and/or the interchain interactions. Since the ferromagnetic coupling is much stronger than the antiferromagnetic one, we interpret the magnetic data in terms of the ferromagnetic dimer model with a weak interdimer antiferromagnetic interaction, using

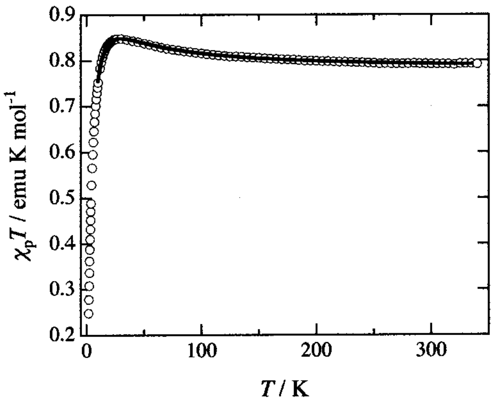

**Figure 3.** Temperature dependence of $\chi_pT$ for TTTA·Cu(hfac)$_2$ in the range 1.8−300 K. The solid curve is the theoretical best fit of eq 1.

$$\chi_p = \frac{4C}{T\{3 + \exp(-2J/k_BT)\} - 2zJ'/k_B} \qquad (1)$$

where $C$ corresponds to the Curie constant, $k_B$ is the Boltzmann constant, $J$ is the ferromagnetic intradimer coupling constant, $J'$ expresses the antiferromagnetic interdimer coupling constant, and $z$ is the number of the nearest neighbors. The derivation of eq 1 is described elsewhere.[17] The solid curve in Figure 3 is the best fit with the parameters: $C = 0.773$ emu K mol$^{-1}$, $J/k_B = 18.5$ K, and $zJ'/k_B = -2.6$ K. The magnetic data are well reproduced by the theoretical curve. It is demonstrated that the cyclic thiazyl radicals can possess a ferromagnetic interaction with Cu(hfac)$_2$ that is as strong as those in the axial coordination compounds of Cu(hfac)$_2$ and nitroxyl radicals.[18]

In summary, we prepared the polymeric coordination complex, TTTA·Cu(hfac)$_2$. TTTA molecules played the role of bidentate bridging ligand, forming an alternating chain. The magnetic data were interpreted in terms of a ferromagnetic dimer with a weak interdimer antiferromagnetic interaction. This work reveals that polycyclic thiazyl radicals are useful as a building block of ferromagnetic coordination compounds.

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**Supporting Information Available:** Crystallographic details for TTTA·Cu(hfac)$_2$ (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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