Long-distance ferromagnetic coupling through spin polarization in a linear heterotrinuclear iron(III)–copper(II)–iron(III) complex derived from 5-ferrocenyl-2-aminotropone†

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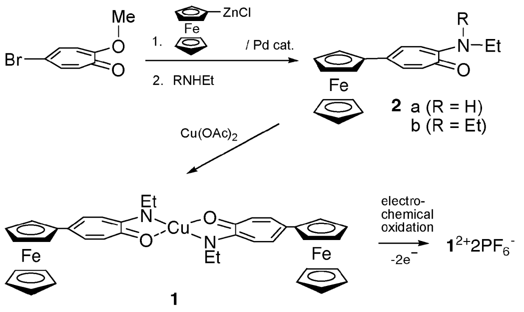
A novel hetrotrinuclear complex composed of two ferrocenium-ion moieties and copper complex of 2-aminotropones showed relatively strong intramolecular ferromagnetic coupling in the solid states owing to spin polarization mechanism.

The design and synthesis of molecular-based magnetic materials have attracted increasing attention. The relatively new research field, named molecular magnetism,[1] was first pioneered with organic π-electron systems[2,3] and soon the objects were expanded into transition metal complexes[4] because of the more stable and diverse magnetic states of transition metals. In the research field, polynuclear complexes with intramolecular long-distance magnetic coupling have actively been investigated.[5] However, despite the significance of ferromagnetic coupling for development of new magnetic materials, the examples of long-distance ferromagnetic coupling within a molecule are still rare, partly due to the lack of new spacers that enable the effective magnetic communication between metal centers.

For long-distance ferromagnetic coupling, a spin polarization mechanism[6] with "non-disjoint" singly occupied molecular orbitals (SOMOs)[7] plays dominant role in organic π-electron systems, while orthogonal magnetic orbitals have often been utilized in metal complexes.[8,9] In the application of spin polarization mechanism to ferromagnetic metal complexes, the spacers used so far have mostly been limited to the *m*-phenylene linkage[10] and related pyrimizine and 1,3,5-triazine ligand,[11] even though the ferromagnetism of the early subjects in the field, *e.g.*, $[Cp^*{}_2Fe]^+[TCNE]^-$[12] was explicated with a spin polarization mechanism.[13] In order to develop new ferromagnetic polynuclear complexes, new design of π-spacers under the concept of spin polarization is important.

As such new π-spacers, we focused on 2-aminotropone. 2-Aminotropone is an amine analogue of tropolone. It was first synthesized from the interest of non-benzenoid aromatics as tropone derivatives.[14] Owing to the contribution of resonance structure of aromatic tropylium ion, basicity of the carbonyl oxygen part are high and the oxygen atom and deprotonated amide can effectively chelate metals.[15] In addition, the chelating arms can conjugate with the π-backbone, which might make the through-bond magnetic coupling by spin-polarization mechanism possible. On the other hand, we are interested in ferrocenium-ion as stable paramagnetic source and have prepared several ferrocene derivatives directly connected to π-conjugated systems.[16] During the course of that work, we found that the two-electron oxidized species of copper(II) complex of ferrocenylaminotropone **1** showed intramolecular ferromagnetic coupling at low temperatures. Here we report the synthesis and properties of $\mathbf{1}^{2+}$ together with the results of theoretical calculations for discussion of the spin polarization mechanism in the ferromagnetism.

As shown in Scheme 1, the precursor ligand of 5-ferrocenyl-2-(ethylamino)tropone (**2a**) was synthesized by Negishi coupling between ferrocenylzinc chloride[16] and 5-bromo-2-methoxytropone[17] followed by the substitution of methoxy group with ethylamine in 80% overall yield. Then the copper(II) complex **1** was obtained quantitatively by the reaction with copper(II) acetate in a mixed solvent of dichloromethane and methanol, which could be recrystallized from THF and isopropyl ether. In contrast, attempted synthesis of the tropolone analogue of **1** was hampered because of the solubility problem. For the preparation of $\mathbf{1}^{2+}$, chemical oxidation was difficult due to the limited solubility of the product, and hence the electrochemical oxidation was conducted to give single crystals of $\mathbf{1}^{2+}\ 2PF_6^-$ when tetra-*n*-butylammonium hexafluorophosphate and dichloroethane were used as electrolyte and solvent, respectively.



Scheme 1 Synthesis of $\mathbf{1}^{2+}\ 2PF_6^-$.

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† Electronic supplementary information (ESI) available: Synthesis, UV-Vis-NIR spectra, ESR spectra, CV, SQUID. CCDC 691675 (**1**), 691674 ($\mathbf{1}^{2+}\ 2PF_6^-$), and 691676 (**2b** ClO_4). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b813944j

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In the X-ray structure of **1** and $\mathbf{1}^{2+}$ $2PF_6^-$¶ (Fig. 1a), the chelating arms show square-planar coordination around the formal Cu(II) atoms with a conformation of Fe···Cu···Fe atoms being linearly arranged. From the comparison of these molecular structures, no remarkable change in the bond lengths and angles upon the two-electron oxidation is observed except for a slight elongation of the Fe–Cp distances, suggesting that the additional positive charge in $\mathbf{1}^{2+}$ is mostly localized on the formal Fe(III) atoms of ferrocenium-ion moieties. As a result, the intramolecular distances between the Fe(III) (or II)···Cu(II) and Fe(III) (or II)···Fe(III) (or II) atoms are almost identical for **1** (8.67 and 17.34 Å) and $\mathbf{1}^{2+}$ (8.77 and 17.53 Å). As concerns the packing structures, unlike the packing of **1** in a herringbone manner, $\mathbf{1}^{2+}$ showed a stacking structure (Fig. 1b), in which the nearest intermolecular Fe(III)···Cu(II) distance (5.17 Å) is shorter than the intramolecular Fe(III)···Cu(II) distance. Nevertheless, the ferromagnetic coupling is obtained intramolecularly as described below.

In electronic absorption spectra, a THF solution of **1** showed a very weak MLCT band at 730 nm (log ε = 2.3) in addition to the absorption band from the ferrocenylaminotropone moiety (λ_{max} (log ε); 409 nm (4.6)). In sharp contrast, an acetonitrile solution of $\mathbf{1}^{2+}$ $2PF_6^-$ showed a very broad absorption in the near-IR region (λ_{max} (log ε); 1230 nm (3.0)). The characteristic broad band is apparently ascribed to the strong π–d interaction between the π-spacer and the Fe(III)·Cu(II) metals, because there is no such absorption band for **1** or $\mathbf{2b}^+$ ClO_4^-‖ (λ_{max} (log ε); 380 nm (4.2), 582 nm (3.5)). On the other hand, the ESR spectrum of **1** in THF showed typical signal pattern for Cu(II) complex with nitrogen ligands ($g_\perp$ = 2.033 (a_N = 1.04 mT), $g_\parallel$ = 2.127 (a_{Cu} = 7.89 mT)), whereas the signal from the Cu(II) part had almost disappeared for $\mathbf{1}^{2+}$ $2PF_6^-$ in acetonitrile at room temperature, indicating the presence of intramolecular exchange interaction between the Cu(II) and Fe(III) atoms. Furthermore, $\mathbf{1}^{2+}$ $2PF_6^-$ both in the solid states and in a frozen acetonitrile solution showed identical quite broad signals ranging from 100 to 500 mT below 40 K, whereas $\mathbf{2b}^+$ ClO_4^- only gave typical ESR spectra of ferrocenium ion.[18] Thus, the characteristic ESR signal of $\mathbf{1}^{2+}$ at low temperatures is ascribed to the magnetic interaction between the Cu(II) and Fe(III) atoms, and the identical signal shape irrespective of the observation conditions suggested the presence of intramolecular magnetic coupling at low temperatures.

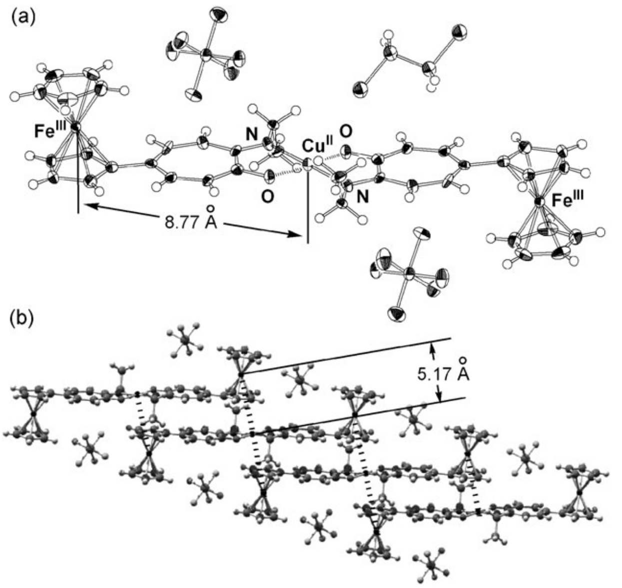

Fig. 1 X-ray structure of $\mathbf{1}^{2+}$ $2PF_6^-$ $C_2H_4Cl_2$. (a) ORTEP drawing (50% probability). (b) Packing structure.

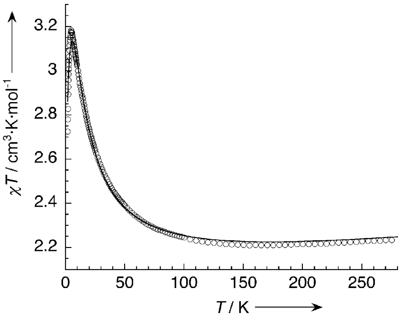

Fig. 2 Thermal dependence of $\chi_M T$ for $\mathbf{1}^{2+}$ $2PF_6^-$; (○) experimental data; (—) fitting curve.

The detailed magnetic properties were examined with SQUID. The magnetic behavior of $\mathbf{1}^{2+}$ $2PF_6^-$ as a $\chi_M T$ *vs.* T plot is shown in Fig. 2. Upon cooling, the $\chi_M T$ values slightly decrease until around 150 K due to the temperature independent paramagnetism (TIP) of ferrocenium-ion moiety, then gradually increase and reach a maximum up to 3.2 emu K mol^{-1} at 4.8 K, and then rapidly decrease until 2 K. These results can be explained that there are a stronger ferromagnetic interaction and a weaker antiferromagnetic interaction between low spin state (S = 1/2) of two Fe(III) atoms and Cu(II) atom (S = 1/2). A good fit to the experimental data was obtained with g = 2.69, J = +12.0 cm^{-1}, J' = −0.05 cm^{-1}, and TIP = 560×10^{-6} emu mol^{-1}.[19] Taking the results of X-ray and ESR analyses into consideration, we concluded that the intramolecular ferromagnetic and intermolecular antiferromagnetic coupling take place despite of the longer Fe(III)–Cu(II) intramolecular distance than the intermolecular distance.

To support the conclusion, the electronic structures of doublet and quartet states of $\mathbf{1}^{2+}$ were estimated by DFT calculations using the X-ray structure.[20] In these calculations, the quartet state (spin densities, Fe(III) 1.1179, Cu(II) 0.6081) was shown to lie below the doublet state (Fe(III) 1.1384, Cu(II) −0.6089) by the energy gap of 97 cm^{-1}. Furthermore, when the spin density distributions was depicted, a precise orbital picture of the ferromagnetic coupling in the quartet state of $\mathbf{1}^{2+}$ was found to be apparent as shown in Fig. 3. In the ferrocenium ion moiety, negative spin densities are induced in the whole Cp ligand by the Fe(III) atom, as in the case of other ferrocenium ions.[13] On the other hand, the nitrogen and oxygen atoms around the Cu(II) metal show a relatively large positive spin distribution due to the contribution of resonance structures between Cu(↑)–N(or O)(↑↓) and Cu(↑↓)–N(or O)(↑). Since the calculated spin density on N (0.1578) is larger than O (0.1140), the resonance between Cu and N atoms is more important principally due to the substantial covalency of the Cu–N bond. As a result, the sign alternation of spin

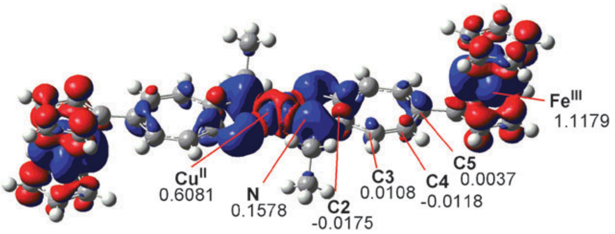

Fig. 3 Calculated spin densities of the quartet state of $\mathbf{1}^{2+}$.

density from the Cu(II) atom through the N, C2–C5, and Cp ring to the Fe(III) atom is in accordance with the spin polarization mechanism of the ferromagnetic coupling, whereas there is a mismatch in the doublet state which restrains Cu(↑↓)–N(or O)(↑) delocalization, judging from the lower spin density on N (−0.0693) and O (−0.0774).

In summary, we have revealed that the novel heterotrinuclear Fe(III)–Cu(II)–Fe(III) complex $\mathbf{1}^{2+}$ $2PF_6^-$ showed a long-distance intramolecular ferromagnetic coupling at low temperatures. From the DFT calculations, the spin polarization mechanism through the π-system of 2-aminotropone and cyclopentadienyl ligand was clearly demonstrated for the ferromagnetism in $\mathbf{1}^{2+}$. As a related example, a long-distance (>6 Å) ferromagnetic coupling (J = +22 cm^{-1}) of a linear trinuclear Cu(II)–Fe(III)–Cu(II) complex by the use of orthogonal magnetic orbitals has once been reported.[9] However, to our knowledge, such a long-distance ferromagnetic coupling in linear trinuclear complex including Cu(II) and Fe(III) centers as reported in the present work has never been attained through spin polarization mechanism. In this context, we have successfully added 2-aminotropone spacer as a potentially versatile new ligand in molecular magnetism.

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Notes and references

¶ Crystal data for **1**. $C_{38}H_{36}CuFe_2N_2O_2$, M = 727.93, monoclinic, a = 20.359(5), b = 9.756(9), c = 8.232(4) Å, β = 98.43(3)°, U = 1617.4(17) Å^3, T = 123 K, space group P2$_1$/c (no. 14), Z = 2, 3731 reflections measured. The final R_1 and $wR(F2)$ was 0.052 and 0.160 ($I > 2\sigma(I)$).
Crystal data for $\mathbf{1}^{2+}$ $2PF_6^-$. $C_{40}H_{40}Cl_2CuF_{12}Fe_2N_2O_2P_2$, M = 1116.82, triclinic, a = 10.197(10), b = 10.402(16), c = 10.513(10) Å, α = 84.50(8), β = 68.16(7), γ = 84.28(8)°, U = 1028(2) Å^3, T = 120 K, space group P-1 (no. 2), Z = 1, 3263 reflections measured. The final R_1 and $wR(F2)$ was 0.063 and 0.146 ($I > 2\sigma(I)$).
‖ Crystal data for $\mathbf{2b}^+$ ClO_4^-. $C_{21}H_{23}ClFeNO_5$, M = 460.70, monoclinic, a = 7.6219(6), b = 24.8096(18), c = 10.8126(8) Å, β = 92.7620(10)°, U = 2042.2(3) Å^3, T = 293 K, space group P2$_1$/n (no. 14), Z = 4, 2941 reflections measured. The final R_1 and $wR(F2)$ was 0.0313 and 0.0836 ($I > 2\sigma(I)$).

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19 Magnetic measurements were carried out on a SQUID magnetometer on single crystals in the range from 2 K to 300 K. The susceptibility curve was fitted using Heisenberg liner-type tri-spin model (S_{Fe1},S_{Cu},S_{Fe2}) = (1/2, 1/2, 1/2) $H = -2J(S_{Fe1}/S_{Cu} + S_{Fe2}/S_{Cu})$.
20 Electronic structure calculations were performed with density functional B3LYP method and the triple-ζ (TZV) basis set by using Gaussian-03 program. The broken-symmetry approach was implemented for the doublet state. The atomic spin densities were obtained by Mulliken population analysis.