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Superparamagnetic Behavior in an Alkoxo-Bridged Iron(II) Cube

Hiroki Oshio,* Norihisa Hoshino, and Tasuku Ito

Department of Chemistry, Graduate School of Science
Tohoku University, Aoba-ku, Sendai 980-8578, Japan

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Metal clusters with superparamagnetic behavior have drawn considerable interest due to their solid-state properties including magnetic hysteresis[1] and quantum tunneling of magnetization.[2,3] Such molecules behave as a single-domain bulk magnet and are called single-molecule magnets.[4] At present the number of single-molecule magnets is limited, and some clusters containing Mn(III,VI),[5] Fe(III),[6] Cr(III),[7] and V(III)[8] ions have been reported to be single-molecule magnets. Among them, the Mn(III,IV) oxo clusters of $[Mn_{12}O_{12}(RCOO)_{16}(H_2O)]$ (Mn_{12}),[9] one of which showed the highest blocking temperature, were extensively studied. To design a single-molecule magnet, the cluster molecule should have a high-spin ground state and the magnetic anisotropy must be an easy-axis type. Fe(II) clusters are certainly a good candidate to be a single-molecule magnet because the magnetically anisotropic Fe(II) ion is in an $S = 2$ high-spin ground state. To the best of our knowledge, no reports of a single-molecule magnet involving an Fe(II) cluster have been published yet.

Transition metal complexes having a cubane structure are a well-studied class of compounds (M_4L_4),[10] in which the four metal ions are bridged by hydroxo, alkoxo, azido, sulfido, or iminato groups.[11] Many alkoxo-bridged Cu(II) and Ni(II) cubanes have been prepared and were reported to have intracluster ferromagnetic interactions with $S = 2$ and 4 spin ground states, respectively.[12] Three Fe(II) cubes have been structurally characterized, and only $[Fe(OMe)(MeOH)(dpm)]_4$ (Hdpm = dipivalolylmethane) was shown to have an $S = 8$ ground state.[13] However, ac magnetic susceptibility measurements have not been reported yet. We report here the first observation of slow magnetic relaxation phenomena, characteristic of the single molecule magnet, in the alkoxo-bridged Fe(II) cube.

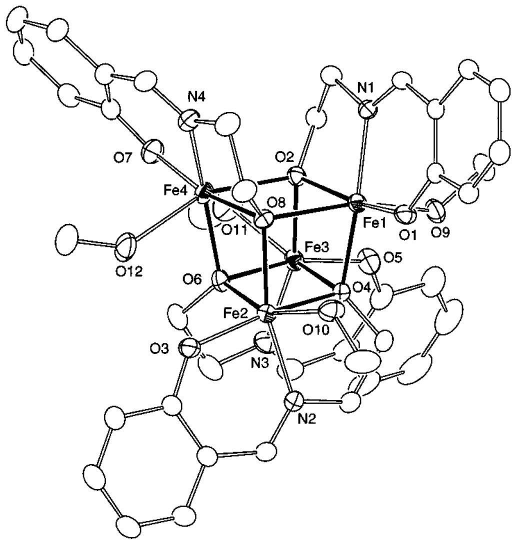

Figure 1. ORTEP representation of **1**. The atoms are drawn with 30% probability thermal ellipsoids.

The reaction of $FeCl_2 \cdot 4H_2O$ with a ligand H_2sae (2-salicylideneamino-1-ethanol)[14] in methanol under strict anaerobic conditions afforded dark blue plates of $[Fe_4(sae)_4(MeOH)_4]$ (**1**) (yield: 35%).[15]The structure of **1** contains a tetranuclear cubane core (Figure 1), of which four iron(II) ions were bridged by μ_3-alkoxo groups, giving an approximately cubic array of alternating iron and oxygen atoms.

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[14] The ligand H_2sae was prepared by the condensation reaction of salicyl aldehyde with 2-aminoethanol.

[15] Crystal data for **1**: ($C_{40}H_{52}Fe_4N_4O_{12}$); dark blue plate (0.2 × 0.2 × 0.3 mm^3), $M = 1004.26$, triclinic $P1$ with $a = 13.3625(7)$ Å, $b = 13.7572(7)$ Å, $c = 14.2004(7)$ Å, $\alpha = 66.538(1)°$, $\beta = 74.973(1)°$, $\gamma = 71.105(1)°$, $V = 2239.9(2)$ Å^3, $Z = 2$, $T = -70$ °C; a total of 8707 (R(int) = 0.0189) unique reflections (3° $< 2\theta <$52°) were measured. Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in calculated positions and refined with isotropic thermal parameters riding on those of the parent atoms. Full-matrix least-squares refinement on F^2 (541 variables) converged to $R1 = 0.0477$ and $wR2 = 0.0959$ (all data).

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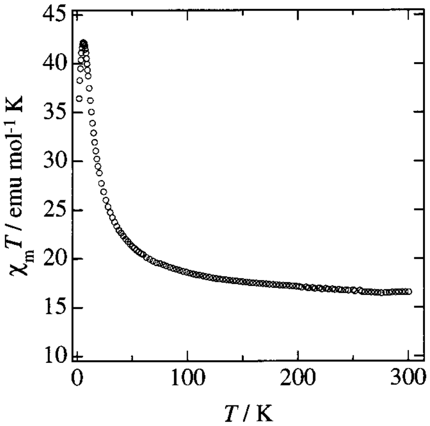

Figure 2. Temperature dependence of the $\chi_m T$ for **1**.

The complex molecule has an idealized $\bar{4}$ axis passing through the middle of Fe1···Fe4 and Fe2···Fe3 vectors, and intracluster metal−metal separations of Fe1···Fe4 and Fe2···Fe3 are 3.3769(6) and 3.4041(7) Å, respectively, which are slightly longer than the other interatomic distances of the iron(II) centers (3.1503(5)−3.1644(7) Å). The coordination geometry about each iron(II) ion is an axially elongated octahedron in which the equatorial sites are occupied by a tridentate sae^{2-} ligand and an alkoxo oxygen atom from the next unit of the cube. The coordination bond lengths with equatorial atoms are in the range of 2.078(2)−2.101(2) Å and a significant tetragonal elongation (2.255(2)−2.343(2) Å) occurs along the trans O−Fe−O bond vector involving methanol and bridging alkoxide. The bridging angles of the Fe−O−Fe bonds, which determine the sign of the magnetic exchange interactions through oxygen bridges, are in the range of 92.37(6)−103.61(7)°.

The temperature dependence of the cluster's magnetic susceptibility was measured in the temperature range 1.8−300 K (Figure 2). At room temperature, the value of $\chi_m T$ is 16.57 emu mol^{-1} K. Upon cooling, $\chi_m T$ increased to a maximum value of 42.19 emu mol^{-1} K at 6 K. This magnetic behavior is indicative of ferromagnetic interactions among the iron(II) centers and predicts an $S = 8$ spin ground state for **1**. A sudden decrease of $\chi_m T$ values below 6 K is due to an inter-cube antiferromagnetic interaction and/or zero-field splitting. The structural analysis showed that the elongated Jahn−Teller axes about each iron(II) ion are O9−Fe1−O8, O6−Fe2−O10, O4−Fe3−O11, and O2−Fe4−O12, and the interatomic distances for Fe1···Fe4 and Fe2···Fe3 are longer than the other pairs. It is supposed that the Fe(II) cube **1** has a magnetic anisotropy, of which D values can be determined by a high-field (HF) EPR measurement.[2a,5c] The contribution of the magnetic anisotropy should be, therefore, included in the analysis of the magnetic data in the lower temperature range. Full analysis of the magnetic data will be presented after the measurement of HF-EPR.

Ac magnetic susceptibility measurements for a polycrystalline sample were performed in the range of 1.8−4.0 K with a 3 G ac field oscillating at 250−1000 Hz. The amplitude of in-phase (χ_m') signals (Figure 1S), which were frequency dependent, increased as the temperature was lowered, reaching the maximum value at 2.0−2.5 K and followed by approaching zero. The out-of-phase (χ_m'') signals (Figure 3) showed a frequency dependence. As the frequency of the ac field is changed from 1000 to 250 Hz, the χ_m'' peak shifted from 2.17 to 1.96 K, while at the lower oscillating frequency of 100 Hz the χ_m'' peak shifted below 1.8 K. The analysis of the ac magnetic susceptibility data gives the value of the energy barrier ΔE to reorientation between two possible directions of magnetizations ($M = 8$ and -8). When the ac oscillating frequency corresponding to the observed peaks at different temperatures was used as the relaxation rate (τ), an Arrhenius plot of ln(τ) vs 1/T gave the activation energy (ΔE) of 28.4 K and a preexponential factor of 2.06×10^{-9} s. It should be noted that magnetic hysteresis was not observed at 1.8 K because of the cube's low blocking temperature ($T_B = 1.1$ K).

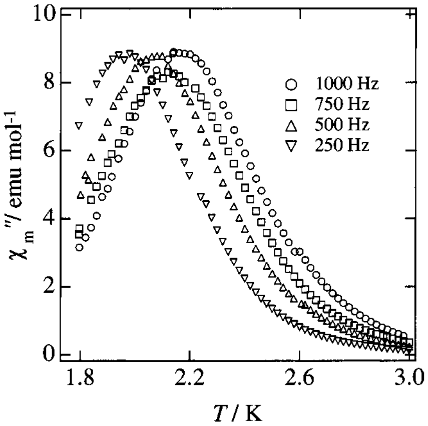

Figure 3. The out-of-phase ac magnetic susceptibility χ''_m vs temperature in a 3.0 G ac field oscillating at the indicated frequencies and with a zero dc field.

The results reported here suggest the possibility of designing a new family of single-molecule magnets. Modifying the Schiff-base ligand can change the redox properties of iron(II) core, which may strengthen the ferromagnetic interactions through the alkoxo-bridge. As well the introduction of distortion in the cube's core may lead to a large magnetic anisotropy.

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Supporting Information Available: χ'_m vs temperature plot plus tables of crystal data, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, hydrogen coordinates, and structure factors for $[Fe_4(sae)_4(MeOH)_4]$ (**1**) (PDF) and an X-ray crystallographic file for the crystal structure determination of $[Fe_4(sae)_4(MeOH)_4]$ (**1**) (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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