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Cobalt single-molecule magnet

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A cobalt molecule that functions as a single-molecule magnet, $[Co_4(hmp)_4(MeOH)_4Cl_4]$, where hmp^- is the anion of hydroxymethylpyridine, is reported. The core of the molecule consists of four Co(II) cations and four hmp^- oxygen atom ions at the corners of a cube. Variable-field and variable-temperature magnetization data have been analyzed to establish that the molecule has a $S=6$ ground state with considerable negative magnetoanisotropy. Single-ion zero-field interactions (DS_z^2) at each cobalt ion are the origin of the negative magnetoanisotropy. A single crystal of the compound was studied by means of a micro-superconducting quantum interference device magnetometer in the range of 0.040–1.0 K. Hysteresis was found in the magnetization versus magnetic field response of this single crystal.
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I. INTRODUCTION

Single-molecule magnets (SMMs) are of great interest because they provide a means to systematically study the chemistry and physics of nanomagnets.[1] They can be considered as slowly relaxing magnetic particles of well-defined size, shape and orientation. A single-molecule magnet has a large-spin ground state with appreciable negative magnetic anisotropy (Ising type), resulting in an energy barrier (DS_z^2) for the reversal of the direction of magnetization. At low temperatures, magnetization hysteresis loops and out-of-phase ac susceptibility signals are seen.

Even though many SMMs have been synthesized, only one molecule has been reported for a transition metal ion with more than five d electrons.[2] If a molecule is to be a SMM, it must have a negative magnetoanisotropy ($D<0$ for the DS_z^2 interaction) and metal ions with $d^n(n>5)$ typically have $D>0$. It is known that for molecules with two or more metal ions that the overall magnetoanisotropy is the tensor projection of the single ion contributions.[3] Theoretically, it is possible for a molecule to have $D<0$ even though the constituent metal ions have single-ion zero-field interactions with $D>0$. In this article we report on a cobalt SMM. It is known that Co(II) ions have $D>0$.

II. EXPERIMENTAL RESULTS

The complex with composition $[Co_4(hmp)_4(MeOH)_4Cl_4]$ (called Co_4), where hmp^- is the anion of hydroxymethylpyridine, was prepared by reacting $Co(H_2O)_6Cl_2$, sodium

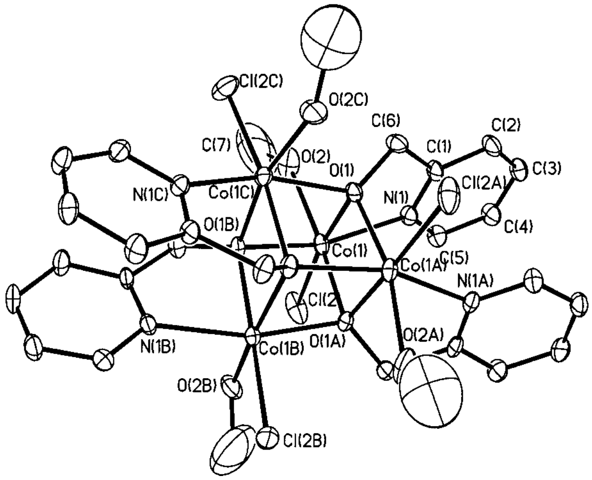

FIG. 1. The structure of the $[Co_4(hmp)_4(MeOH)_4Cl_4]$ complex. Selected distances (Å) are: Co(1)–O(1B) 2.090(2), (2.083(2)), Co(1)–O(1) 2.144(2) (2.129(2)), Co(1)–N(1) 2.121(2) (2.102(2)), Co(1)–O(1a) 2.076(2) (2.067(2)), Co(1)–Cl(2) 2.3758(9) (2.3827(8)), Co(1)–O(2) 2.189(3) (2.163(2)).

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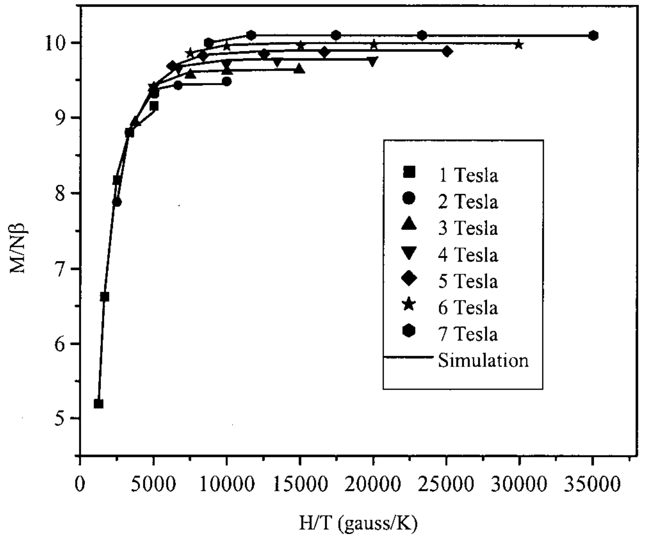

FIG. 2. Plot of reduced magnetization measurement with sample aligned with magnetic field and the simulation curve.

methoxide (MeONa), and hydroxymethylpyridine (1:1:1 ratio) in methanol. The single crystal x-ray structure of this complex has been determined (Fig. 1). The Co_4 molecule crystallizes in tetragonal space group $I42d$[4] as the similar Ni_4 molecule.[5] The core of this molecule consists of four Co(II) ions and four oxygen atoms ($^{-}$OR) from the hmp^{-} ligands. Each Co(II) is six coordinate with one pyridine N atom, one MeOH ligand, one Cl^{-} ligand and three $^{-}$OR atoms from the hmp ligands. Examination of the crystal packing indicates that the Co_4 molecules are reasonably well isolated. Neither the hmp^{-} planar pyridine ligands nor the Cl^{-} ligands on one molecule interact significantly with the same ligands on nearby molecules. Intermolecular magnetic exchange interactions are minimal. The geometry of this complex has S4 site symmetry for an individual molecule in the crystal and this suggests that the orthogonal hard-axis alignment[6] for the cubane-type metal cluster is suitable to analyze the magnetic susceptibility data.

The magnetic susceptibility (χ_M) of Co_4 has been measured in a 10 kG dc field and in a 1.0 G ac field oscillating at 1000 Hz. The $\chi_M T$ value is 11.8 $cm^3\,mol^{-1}\,K$ at 300 K and remains essentially constant as the temperature is decreased until ~30 K, below which it increases to a maximum value of 12.4 $cm^3\,mol^{-1}\,K$ at 15 K before rapidly decreasing to 5.4 $cm^3\,mol^{-1}\,K$ at 2 K. The abrupt decrease of the $\chi_M T$ value at low temperatures may be caused by either zero-field splitting or weak intermolecular antiferromagnetic coupling. It is clear that strong intermolecular ferromagnetic exchange interactions are not present and, therefore, the magnetization hysteresis that is observed (*vide infra*) is not due to ferromagnetic coupling between Co_4 molecules. The out-of-phase ac susceptibility (χ''_m) is less than 0.01 $cm^3\,mol^{-1}$ at temperatures above 3.5 K and substantially increases to 0.16 $cm^3\,mol^{-1}$ as the temperature is decreased to 1.8 K. The substantial increase of the out- of-phase ac signal suggests that the Co_4 molecule has an appreciable energy barrier for reversing its magnetization.

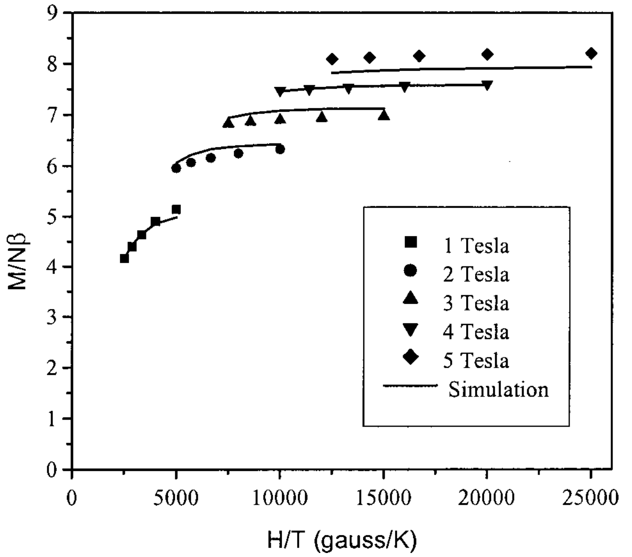

FIG. 3. Plot of reduced magnetization measurement of randomly oriented powder sample and the simulation curve.

The Co_4 complex was determined to have a large ground state spin by an analysis of the two types of low-temperature, variable-field magnetization data depicted in Figs. 2 and 3. Figure 2 gives data for a sample aligned with the magnetic field, whereas Fig. 3 illustrates the random powder sample data. The simulation of both types of data sets was carried by employing the spin Hamiltonian for an orthogonal hard-axis-type alignment model[6] as given in Eq. (1):

$$\hat{H}=-2J_0(\hat{S}_2\hat{S}_3+\hat{S}_4\hat{S}_1+\hat{S}_1\hat{S}_3+\hat{S}_2\hat{S}_4)-2J_1(\hat{S}_1\hat{S}_2+\hat{S}_3\hat{S}_4)$$
$$+D'(\hat{S}_{1x}^2+\hat{S}_{2y}^2+\hat{S}_{3x}^2+\hat{S}_{4y}^2)+g\mu_B B\hat{S}_z. \tag{1}$$

In this equation S_n (n=1,2,3,4) is the spin on each metal atom n, S_{nj} ($j=x,y,z$) is the component of S_n in the j direction, D' is the axial zero-field splitting for each individual metal atom, and J_0 and J_1 are the exchange coupling constants. The magnetization of a polycrystalline sample of Co_4 is given by the Van Vleck Eq. (2):

$$M=N\times\left[\sum(-\partial E_i/\partial H)\exp(-E_i/kT)/\sum\exp(-E_i/kT)\right]. \tag{2}$$

In the above equation N is Avogadro's number, k is the Boltzmann constant and $\partial E_i/\partial H$ is the change in energy of the ith level in response to a change in the magnetic field. Full matrix diagonalization of the Hamiltonian matrix was carried out in the uncoupled basis set. The zero-field splitting in the ground state of the Co_4 molecule (D) is related to the single-ion zero-field parameter (D') as given in Eq. (3):

$$D\approx-(1/11)D'. \tag{3}$$

The best simulation was found with $g=1.97$, $D'=44.2$ K, $J_0=5.15$ K, $J_1=-6.95$ K for Fig. 2, and $g=2.12$, $D'=44.8$ K, $J_0=4.77$ K, $J_1=-7.80$ K for the data in Fig. 3. These two sets of parameters lead to the result that $S_T=6$ (S_T is the total spin for the whole molecule) and the resultant

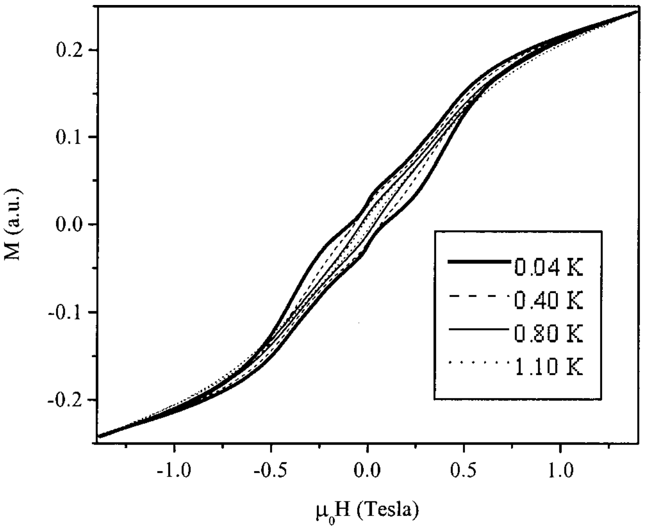

FIG. 4. Plot of hysteresis loop with constant scanning rate (0.140 T/s) at four different temperatures.

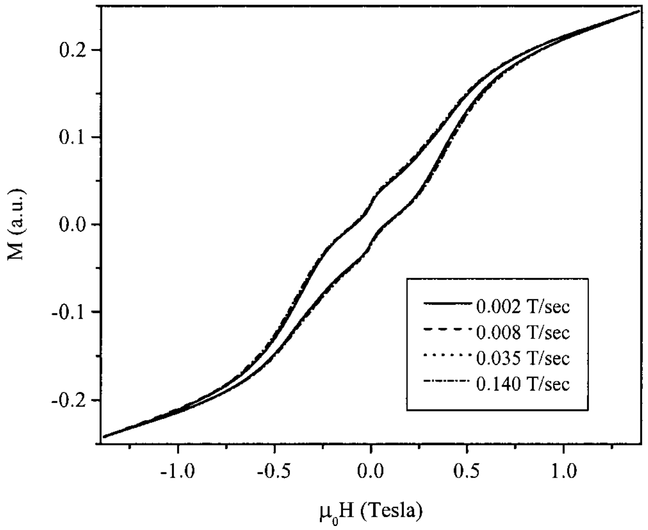

FIG. 5. Plot of hysteresis loop with different scanning rates at a constant temperature (0.04 K).

axial zero-field splitting for the whole molecule is $D \cong -4$ K. The above calculations assume that the Co–Co magnetic exchange interactions are isotropic. It is likely these exchange interactions are anisotropic. A more involved theoretical analysis is needed to evaluate the effects of exchange anisotropy.

We used the micro-superconducting quantum interference device technique[7] to measure magnetization hysteresis loops of a single crystal for complex **1** at different temperatures and field sweep rates. The field was roughly aligned with the easy axis of magnetization. Figure 4 shows hysteresis loops with a constant field sweep rate of 0.14 T/s at different temperatures ranging from 0.04 to 1.1 K. The loops present hysteresis for temperatures below about 1.2 K which increase rapidly upon decreasing the temperature. The temperature dependence and area within the hysteresis loop indicate that this molecule has considerable negative magnetoanisotropy as expected for a SMM. On the other hand, Fig. 5 shows hysteresis loops at a constant temperature of 0.04 K for different field scanning rates between 0.002 and 0.140 T/s. The hysteresis loops only weakly depend on the field scanning rate which suggests that resonant quantum tunneling is hindered by small intermolecular exchange interactions. More studies are in progress to improve the alignment of the fields and to understand better the fine structure of the hysteresis loops.

III. CONCLUSION

The Co_4 molecule has been found to be a single-molecule magnet. This establishes that this phenomenon can occur with molecules comprised of metal atoms with single-ion zero-field interactions (DS_z^2) where $D>0$. Further theoretical analyses are needed to evaluate the effects of magnetic exchange anisotropy.

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