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Magnetic properties of a noninterpenetrating chiral porous cobalt metal-organic framewok

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Noninterpenetrating chiral porous cobalt metal-organic framework built from the coplanar triangular H_3TATB ligands has been synthesized under solvothermal conditions. X-ray analysis revealed the compound crystallized in the chiral space group either $P4_132$ or $P4_332$, and adopted a trimetallic "hourglass" secondary building unit, in which there are two terminal T_d-Co atoms and one central O_h-Co with T_d-Co and O_h-Co distance about 3.604 Å. Paramagnetic behavior is observed throughout the measured temperature range of 2–300 K. Assuming a uniform isotropic interaction between the nearest neighbor Co atoms, susceptibility of the trinuclear Co^{2+} linear chain has been calculated by following Van Vleck's quantum model for spin-spin couplings. The resultant fit to the data indicates an antiferromagnetic Co–Co interaction in the molecule, with coupling strength $J \sim -6.2 \times 10^{-16}$ erg, $\theta \sim -16$ K. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2714674]

INTRODUCTION

Metal-organic frameworks, which consist of metal-oxide clusters connected by organic linkers, have attracted great attention due to their intriguing topologies and various potential applications in catalysis,[1] gas storage,[2,3] and magnetism.[4,5] In particular, the ability to adopt a variety of transition metal elements into the framework may lead to materials with interesting magnetic properties. By tuning the distance between the magnetic ions via bridging ligands, this kind of materials also serves as unique candidates for modeling the magnetic spin-spin interaction through the mediating agents on quantum mechanism level.[6] Herein, we present our study on a metal-organic framework fabricated by using the trimetallic Co "hourglass" as the building block. X-ray shows that these frameworks form a porous chiral architecture network in either $P4_132$ or $P4_332$ space symmetry. Magnetic measurements revealed that the compound is paramagnetic down to 2 K. Magnetic susceptibility has also been calculated according to Kambe's quantum approach,[7,8] and it shows the presence of potential antiferromagnetic interaction among the Co^{2+} ions with coupling constant $J \sim -6.2 \times 10^{-16}$ erg.

EXPERIMENT

The complex was synthesized under typical solvothermal condition. A mixture of H_3TATB(4, 4′,4″-s-triazine-2,4,6-triyl-tribenzoate) ligand (0.01 g, 2.26×10^{-5} mol) and $Co(NO_3)_2 \bullet 6H_2O$ (0.025 g, 8.6×10^{-5} mol) in 1.5 ml dimethylacetamide (DMA) was sealed in a Pyrex tube and heated to 120 °C (1 °C/min) at which it stayed for 48 h, and then cooled to 35 °C with the decreasing rate of 0.1 °C/min. The resultant purple crystals were washed with DMA twice to give the pure compound with formula $Co_3(TATB)_2(H_2O)_2 \cdot 2DMA \cdot 3H_2O$.

The magnetic properties of the molecule was measured by Quantum Design physical property measurement system (PPMS). In this work two operation modes were used. For magnetization curve measurement, we used the dc or extraction method, where the magnetic sample itself moves during each measurement. For susceptibility measurement, we use ac mode, where instead of moving the sample an alternating ac field is applied to the sample region to generate inductions. The system can be operated in the temperature range of 300–2 K with a magnetic field up to 9 T. The sensitivities of the ac and dc measurements are up to $\sim 1 \times 10^{-8}$ and 2.5×10^{-5} emu, respectively.

RESULTS AND DISCUSSIONS

Single x-ray analysis revealed that the compound crystallized in either $P4_132$ or $P4_332$. The frameworks adopt a trimetallic hourglass secondary building unit (SBU), in which there are two terminal T_d-Co atoms and one central O_h-Co [Fig. 1(a)] with neighboring Co atoms separated by 3.604 Å. The T_d-Co coordinates with three different carboxylate groups and one terminal water molecule pointing toward channels, while the O_h-Co binds to six different carboxylates. In the framework, every ligand pair is bound to

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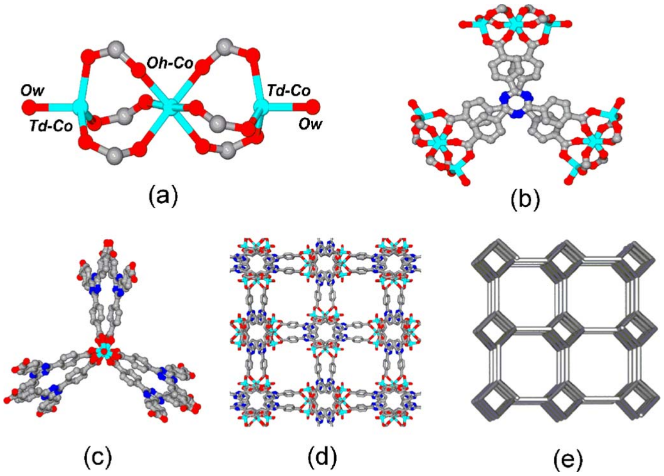

FIG. 1. (a) The trimetallic Co "hourglass" building block. (b) TATB staggered pair connecting with three hourglass SBU in a clockwise arrangement. (c) The right-handed propeller arrangement around the hourglass SBU. (d) 4_3 helical channels of 1.84 nm along tetragonal edge packed from *b* axis. (e) The chiral (10, 3)-a net.

three hourglass SBUs in a clockwise (or counterclockwise) arrangement [Fig. 1(b)] and every SBU connects with three ligand pairs to form a right-handed (or left-handed) propeller [Fig. 1(c)]. The hourglass SBUs are extended by the TATB ligand pairs to form a noninterpenetrated (10, 3)-a framework [Figs. 1(d) and 1(e)], which consists of channels possessing 4_3 or 4_1 and 2_1 symmetry along the three orthogonal directions.

In order to understand the magnetic properties of this molecule, magnetic susceptibility was measured in the temperature range of 300–2 K. During the measurement, a constant magnetic field (~1000 Oe) was applied along with an alternating ac field (4 Oe, 10 kHz). Figure 2 shows the ac susceptibility as a function of temperatures. With decreasing temperatures, initially the susceptibility increases slightly and then dramatically when approaching 2 K. Within the measured temperature range the system only exhibits paramagnetism. The inverse susceptibility as function of temperature ($1/\chi$ vs T) is plotted in the figure as an inset. The solid line of the inset is a theoretical fit, which will be discussed in the following.

The magnetic core of the framework is the Co "hourglass" building block. As seen from Fig. 1(a), it has three Co^{+2} ions ($S=3/2$) connected via organic bridging agents to form an open-end linear chain. The separation between adjacent Co is 3.604 Å. It is believed that the orbit contribution from the two tetrahedral $\mathrm{Co}^{+2}(T_d{:}d^7)$ is quenched, while the central octahedral $(O_h{:}d^7)\mathrm{Co}^{+2}$ may retain some orbit contributions as it supposes to have an unquenched orbit T term under octahedral crystal field.[9] However, the effective moment obtained by fitting the high temperature part of the susceptibility data shows a smaller value ($\sim 4.5\mu_B$) than that of bulk Co^{2+} ($\sim 4.8\mu_B$), indicating it may be a reasonable approximation to consider the spin-spin interaction only when calculating the temperature dependence of the susceptibility of the molecule at low temperatures. Assuming an isotropic coupling, the Co–Co interaction then can be simplified as $J_{12}=J_{23}=J$, and $J_{13}=0$. The Hamiltonian of such finite Heisenberg system can be written as

$$\hat{H}=-2J(\hat{S}_1\cdot\hat{S}_2+\hat{S}_2\cdot\hat{S}_3)-g\mu_B H\cdot\hat{M}_{S_T}.$$

By following the spin vector model, the eigenvalues can be obtained as[8]

$$E(S_T)=-J[S_T(S_T+1)-S^*(S^*+1)-S(S+1)] \\ -g\mu_B H M_{S_T},$$

where $\hat{S}_1=\hat{S}_2=\hat{S}_3=\hat{S}$, $\hat{S}^*=\hat{S}_1+\hat{S}_2$, and $\hat{S}_T=\hat{S}^*+\hat{S}_3$. For $S=3/2$, the total spin S_T can take values of 9/2, 7/2, 5/2, 3/2, and 1/2.

The magnetic susceptibility at a given temperature can be calculated by considering a Boltzmann distribution of the field induced magnetic moments over all populated energy levels $E(S_T)$. It can be expressed as[8]

$$\chi=-\frac{N}{H}\sum\frac{\partial E}{\partial H}e^{-E/kT}\Bigg/\sum e^{-E/kT}$$

$$=\frac{Ng^2\mu_B^2}{3kT}\,\frac{\sum_{S_T}S_T(S_T+1)(2S_T+1)e^{-E(S_T)/kT}}{\sum_{S_T}(2S_T+1)e^{-E(S_T)/kT}},$$

where N is the number of molecules per mole, g the g factor, and k the Boltzmann constant. By calculating the above summations, we find the susceptibility

$$\frac{Ng^2\mu_B^2(165+84e^{3x}+35e^{6x}+94e^{9x}+35e^{10x}+10e^{11x}+e^{14x}+10e^{15x}+35e^{16x}+e^{18x}+10e^{21x})}{4kT(5+4e^{3x}+3e^{6x}+6e^{9x}+3e^{10x}+2e^{11x}+e^{14x}+2e^{15x}+3e^{16x}+e^{18x}+2e^{21x})},$$

where $x=-J/kT$.

The theoretical calculation is shown in the inset of Fig. 2 as a solid line. Here, J is the fitting parameter, and the g factor is also left open in order to accommodate any effect from the unquenched orbital angular momentum, though it was believed that the spin-orbital coupling is minimum in comparing to the spin-spin interaction in general.[8] The mass is also set to be slightly adjustable due to solvent left in the porous structures, which may incur up to 10% uncertainty of the molecular mass. The best fit gives a $J\sim-6.8$

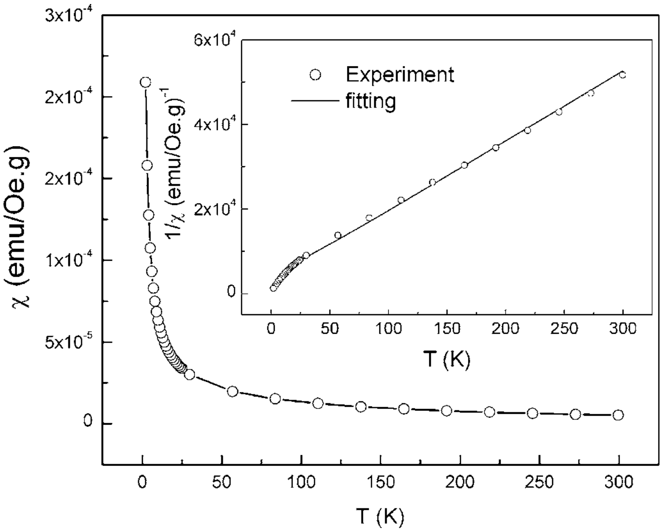

FIG. 2. Susceptibility as function of temperature. Inset shows the $1/\chi$ vs T curve along with a theoretical fitting.

$\times 10^{-16}$ erg or ~ -5 K, and $g \sim 2.2$. The larger than 2 of the g value indicates that the orbit might have slight influence on the effective moment as it is not totally quenched, but as an approximation the fitting gives reasonable agreement to the experimental data. In order to compare with Weiss law, the susceptibility expression can be expanded, which at high temperatures simplifies to

$$\chi = \frac{Ng^2\mu_B^2}{4kT}\left[\frac{15}{1+(10/3)x}\right].$$

In comparison with the classical Weiss law, and the Weiss temperature here is related to the coupling by $\theta = (10/3)\ J/k$, which is about −16 K. The negative value of θ does indicate the existence of antiferromagnetic coupling between the neighboring Co^{2+} ions, though no real antiferromagnetic phase transition occurs in the measured temperature range.

On the other hand, we can also rewrite the susceptibility as $(N\mu_B^2/3kT)\ 3g^2/4f(x)$. It is reminiscent of the Langevin paramagnetic theory of low temperature and $(3g^2/4)f(x)$ corresponds to the square of the effective magnetic moment in the Langevin expression. The effective moment as a function of temperature is plotted in Fig. 3. As seen, the effective moment at 2 K is about $4.2\mu_B$, and it increases gradually to approach saturation when increasing temperatures. This can be understood as follows.[10,11] At low temperatures the system remains mostly in the ground state, which corresponds to the minimum value for the magnetic quantum numbers for a negative J, and when increasing temperatures all spin states with larger quantum numbers will be populated according to the statistical distribution. Magnetization curves at low temperatures (2 K) has also been measured and it shows typical Langevin paramagnetic behavior. The magnetization curve approaches saturation gradually with increasing field.

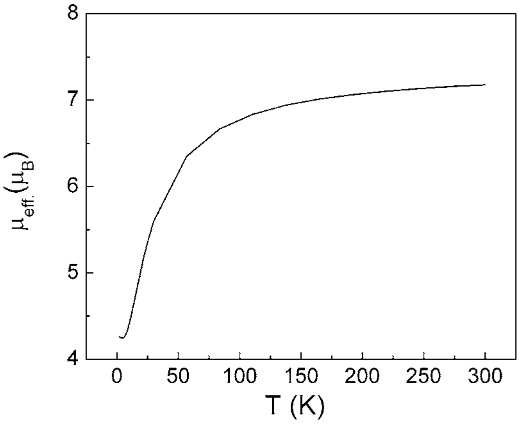

FIG. 3. The effective magnetic moment of the Co-linear chain as function of temperature derived from the Van Vleck quantum model.

CONCLUSION

In conclusion, a chiral porous cobalt metal-organic framework with large channel size has been reported. Magnetic susceptibility measurements indicated that the compound exhibits paramagnetic properties within measured temperature range (2–300 K), though antiferromagnetic coupling is existent between neighboring Co ions. The spin-spin coupling parameter is determined to be $J \sim -6.8 \times 10^{-16}$ erg and the Weiss temperature $\theta \sim -16$ K.

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