

## Cobalt(II) Citrate Cubane Single-Molecule Magnet

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An investigation of the magnetic properties of the cobalt(II) citrate cubane  $[\text{C}(\text{NH}_2)_3]_8\{\text{Co}_4(\text{cit})_4\} \cdot 4\text{H}_2\text{O}$  reveals that the cluster is a new cobalt(II) single-molecule magnet, with an energy barrier to reorientation of the magnetization,  $\Delta E/k_B = 21$  K, and  $\tau_0 = 8 \times 10^{-7}$  s. The compound displays distinct, frequency-dependent peaks in the out-of-phase ( $\chi''$ ) component of the ac magnetic susceptibility and magnetization versus field hysteresis loops that are temperature and sweep rate dependent. The hysteresis loops collapse at zero field due to very fast quantum tunneling of the magnetization (QTM).

## Introduction

In the field of single-molecule magnets (SMMs), an objective of considerable importance is the synthesis of new clusters possessing greater barriers to the reorientation of the magnetization.<sup>1</sup> The height of the energy barrier ( $\Delta E$ ) varies with the square of the spin ( $S$ ) and linearly with the axial zero-field splitting (ZFS) parameter ( $D < 0$ ) via the equation  $\Delta E = S^2|D|$ , or  $\Delta E = (S^2 - 1/4)|D|$  for an integer or noninteger spin-ground state, respectively. Efforts to increase the barrier height have targeted the synthesis of clusters containing larger numbers of metal centers to increase  $S$ , the use of metals with a large anisotropy to increase  $D$ , or by using a directed synthesis approach toward specific cluster geometries.<sup>2</sup> A large number of metal centers do not guarantee a large molecular  $S$ : one approach is to have a cluster topology that provides ferromagnetic interactions such as a metal–oxo cubane structure that can promote ferromagnetic interactions via superexchange.

Metal–oxo cubane structures often appear as structural elements in clusters produced by self-assembly from complex inorganic reaction systems. This is illustrated by the work of Aromí et al.<sup>3</sup> on the cobalt-pivalate system that offers a

wide variety of products including  $\text{Co}_2$ ,  $\text{Co}_4$ ,  $\text{Co}_5$ ,  $\text{Co}_6$ ,  $\text{Co}_7$ , and  $\text{Co}_{14}$  clusters. The authors propose a reaction scheme based on the assembly of small binuclear units and stepwise addition of cobalt(II) ions to form cubane units. These can then be further enlarged, eventually allowing the formation

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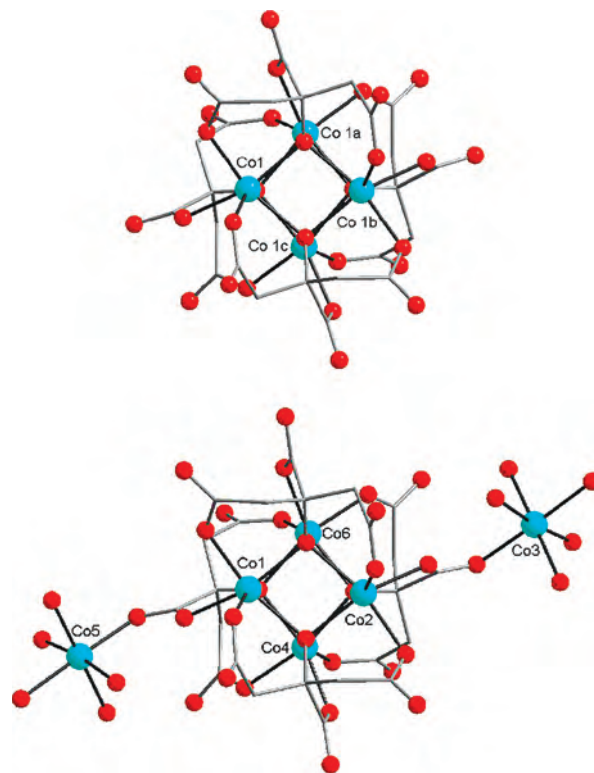
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of stacked, face sharing di- and tri- cubane units. The use of pivalate in conjunction with 8-hydroxyquinaldine gives a discrete cubane with isostructural products using nickel(II) or cobalt(II).<sup>4</sup> In this case, both cubanes show overall antiferromagnetic coupling. The specific geometry of the cubane has a marked effect on the nature of the interactions as illustrated by magnetostructural correlations such as those of nickel(II) cubanes by Halcrow et al.<sup>5</sup> Ni<sub>4</sub> cubanes can function as SMMs, such as the cluster family reported by Yang et al.,<sup>6</sup> which have  $S = 4$  ground states and exhibit interesting exchange bias features. Exchange bias has also been studied in detail for dimers of Mn<sub>4</sub> cubane SMMs.<sup>7</sup> The effect of cubane structural geometry on cluster magnetism is elegantly illustrated by the ferrous cubes synthesized by Oshio et al.<sup>8</sup> Here, the  $D$  parameter can be tuned by adjusting the bite of the coordinating ligand and hence the local geometry at the iron(II) centers.

In comparison to manganese-based SMMs, the field of cobalt(II) SMMs is at early stage of development. The first cobalt-based SMM was a metal-oxo cubane and was reported by Yang et al. in 2002.<sup>9</sup> Since then, slow magnetic relaxation has been observed in a cobalt(II) heptanuclear disk cluster,<sup>10</sup> an octanuclear phosphonate cage,<sup>11</sup> along with mixed metal examples such as spherical Co-W/Mo octacyanometallate-based SMMs<sup>12</sup> and a linear trinuclear Co-Gd-Co cluster.<sup>13</sup> Other recent developments include a mixed-valence heptanuclear cobalt SMM with  $C_3$  symmetry produced in our group,<sup>14</sup> a Co<sub>12</sub> SMM consisting of three metal-oxo cubanes in a triangular arrangement templated by a central nitrate anion and a mononuclear Co(II) SMM.<sup>15</sup>

We have a long-standing interest in the chemistry of cobalt(II) and nickel(II) with the citrate ligand [C(O<sup>-</sup>)(CO<sub>2</sub><sup>-</sup>)(CH<sub>2</sub>CO<sub>2</sub><sup>-</sup>)<sub>2</sub> = cit<sup>4-</sup>] that can promote cubane formation.<sup>16</sup> In 2003, we reported a hexanuclear cobalt(II) citrate SMM [NMe<sub>4</sub>]<sub>3</sub>Na{Co<sub>4</sub>(cit)<sub>4</sub>[Co(H<sub>2</sub>O)<sub>5</sub>]<sub>2</sub>}·11H<sub>2</sub>O, which consists of a central {Co<sub>4</sub>(cit)<sub>4</sub>}<sup>8-</sup> cubane with two peripheral cobalt(II) centers.<sup>17</sup> The cobalt(II) citrate cubane [C(NH<sub>2</sub>)<sub>3</sub>]<sub>8</sub>-



**Figure 1.** Structural comparison of the anions found in [C(NH<sub>2</sub>)<sub>3</sub>]<sub>8</sub>-{Co<sub>4</sub>(cit)<sub>4</sub>}·4H<sub>2</sub>O (upper) and [NMe<sub>4</sub>]<sub>3</sub>Na{Co<sub>4</sub>(cit)<sub>4</sub>[Co(H<sub>2</sub>O)<sub>5</sub>]<sub>2</sub>}·11H<sub>2</sub>O (lower) (ball and stick representation with cobalt(II) cyan; oxygen, red; carbon, gray; hydrogen, omitted for clarity).

{Co<sub>4</sub>(cit)<sub>4</sub>}·4H<sub>2</sub>O (**1**) was recently reported to have a nonmagnetic ground state.<sup>18</sup> Because this cubane has the same structure as the core of the Co<sub>6</sub> SMM (Figure 1) and due to the close correlation of structure and magnetic properties, we would have expected the discrete {Co<sub>4</sub>(cit)<sub>4</sub>}<sup>8-</sup> cubane to function as an SMM. Hence, we synthesized our own samples to further investigate the magnetic properties, and observed SMM behavior, both by ac susceptibility and hysteresis measurements as we had anticipated.

## Experimental Section

All reagents were obtained from commercial suppliers and used as received, and all syntheses were carried out under aerobic conditions.

**Synthesis.** [C(NH<sub>2</sub>)<sub>3</sub>]<sub>8</sub>{Co<sub>4</sub>(cit)<sub>4</sub>}·4H<sub>2</sub>O (**1**). To a solution of citric acid monohydrate (0.55 g, 2.6 mmol) in water (50 mL) was added a solution of Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.76 g, 2.6 mmol) in water (50 mL) followed by a solution of guanidinium carbonate (1.87 g, 10.4 mmol) in water (50 mL). The solution was then left to stand overnight, producing purple crystals, which were air-dried. Powdered samples were found to be slightly hygroscopic and analyzed as the pentahydrate. Anal. Calcd (found) for C<sub>32</sub>H<sub>74</sub>Co<sub>4</sub>N<sub>24</sub>O<sub>33</sub>: C, 24.65 (24.53); H, 4.78 (4.57); N 21.56 (21.57). Selected IR data (cm<sup>-1</sup>): 3330 (m), 3136 (m), 1656 (s), 1605 (m), 1579 (m), 1536 (s), 1426 (m), 1378 (s), 1233 (m), 1082 (w), 958 (m), 923 (m), 849 (m).

**Spectroscopy.** IR measurements were recorded on a Jasco FT/IR-4100 equipped with a Pike Technologies MIRacle ATR.

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Electronic spectra were recorded on samples dispersed in a KBr disk on a Shimadzu UV-3101PC with Displex cooling to  $\sim 20$  K. A baseline correction has been applied to the absorption spectrum.

**X-ray Crystallography.** The identity of the bulk sample was confirmed by powder diffraction at 130 K on a Bruker d8 diffractometer using Cu K $\alpha$  radiation (Supporting Information). The unit cell dimensions of several single crystals were also confirmed on a Bruker APEXII diffractometer using Mo K $\alpha$  radiation at 100 K [expected (130 K data from CSD reference CEHVAN)  $a = 16.1224(8)$  Å,  $c = 11.5088(11)$  Å,  $V = 2991.5(4)$  Å $^3$ ; found (100 K data)  $a = 16.09$  Å,  $c = 11.55$  Å,  $V = 2990$  Å $^3$ ].

**Magnetic Properties.** Magnetic measurements were made on samples of mass ca. 20 mg consisting of single crystals, which were lightly ground to give a randomly oriented polycrystalline sample and loaded into a gelatin capsule. Samples were restrained in eicosane to prevent torquing. The data were measured using a Quantum Design MPMS XL SQUID magnetometer and (for high frequency ac susceptibility, using zero dc field with 3 G ac drive field) a Quantum Design PPMS magnetometer. A diamagnetic correction of  $6.24 \times 10^{-4}$  cm $^3$  mol $^{-1}$  has been applied to the dc susceptibility data. Hysteresis loops were collected on a single crystal of **1** using a micro-SQUID with the field applied along the easy axis of magnetization of the crystal.

## Results and Discussion

**Synthesis.** The product formed rapidly from the reaction conditions reported by Hudson et al.,<sup>18</sup> however working at half-concentration produced samples with a greater number of large, well-formed single crystals. The rapid formation of the product is presumably a consequence of the extensive hydrogen-bonding network present in the crystal lattice. Further investigation of the cobalt(II)/citrate/guanidinium reaction system suggests that the stability of the Co $_4$  cubane gives little synthetic flexibility, and the cubane forms regardless of reactant ratios.

It is interesting to note that this discrete cubane can be obtained by simply changing the tetramethylammonium counterions present in our Co $_6$  reaction system for guanidinium.<sup>17</sup> This highlights the important role of the counterions in such self-assembly reactions and their ability to vary the product obtained, as we have previously reported for the Co $_6$  citrate reaction system at lower pH.<sup>19</sup>

**Structure.** A structural comparison of the {Co $_4$ (cit) $_4$ } $^{8-}$  anion with the previously reported Co $_6$  SMM anion {Co $_4$ (cit) $_4$ [Co(H $_2$ O) $_5$ ] $_2$ } $^{4-}$  is shown in Figure 1. In both cases, the citrate alkoxide group provides the corner bridging oxygen of the cubane, with the citrate carboxylate arms capping the cobalt(II) centers. The short  $\alpha$ -carboxylate arm of citrate imparts a twisted trigonal-prismatic geometry to the six coordinate metal centers, and in the case of Co $_6$  also acts an oxygen coordination site for the two peripheral [Co(H $_2$ O) $_5$ ] $^{2+}$  units. The bridging angles and bond distances in the central cubane of the two anions are similar. In **1** the Co–O–Co angles are in the range 97.18–99.24° with Co–O bond lengths of 2.090–2.136 Å, and in Co $_6$  the angles are in the range 96.46–100.33° with Co–O bond lengths of 2.070–2.142 Å.

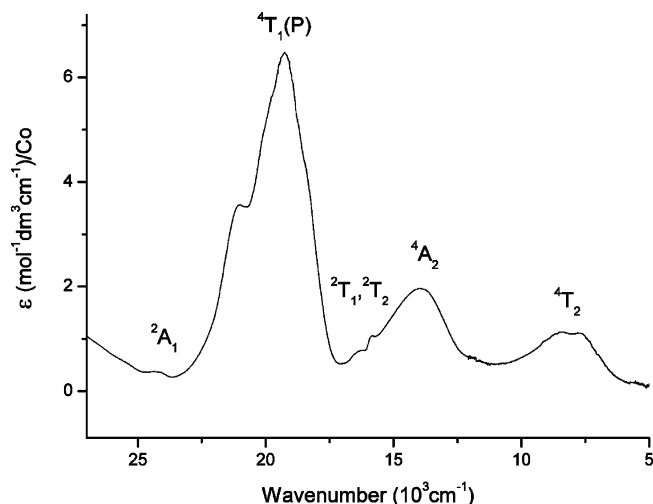


Figure 2. Solid-state electronic spectrum of **1** at 20 K.

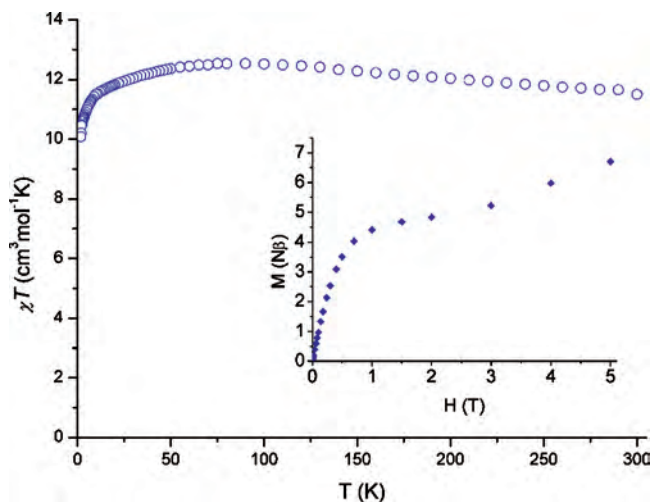
**Spectroscopy.** The electronic spectrum of **1** dispersed in a KBr disk at  $\sim 20$  K is shown in Figure 2. The most striking feature of the spectrum is the large intensity of the  ${}^4T_1 \rightarrow {}^4A_2$  transition, which is very weak in most octahedral or pseudo-octahedral Co(II) compounds.<sup>20</sup> The cobalt centers in the cubane have  $C_1$  symmetry and the highest reasonable symmetry description is distorted  $C_3$ . In  $C_3$  symmetry, the ground and excited  ${}^4T_1$  states and the  ${}^4T_2$  state all split into  ${}^4E$  and  ${}^4A$  states. With either a  ${}^4A$  or  ${}^4E$  ground state, the  ${}^4A({}^4A_2)$  transition becomes allowed, acquiring intensity by mixing (principally) with the  ${}^4A({}^4T_1(P))$  state.

Extracting the values of  $\Delta_o$  and  $B$  for such distorted species is of limited value. However, due to the clear appearance of the  ${}^4T_1 \rightarrow {}^2T_1, {}^2T_2$  transitions,  $B$  can be accurately found. The best fit values of  $\Delta_o = 8150$  cm $^{-1}$  and  $B = 840$  cm $^{-1}$  reproduce the energies of all of the transitions fairly well with the exception of the  ${}^4T_1 \rightarrow {}^4A_2$  transition, which is slightly overestimated. This is consistent with its energy being lowered due to mixing with the  ${}^4A({}^4T_1(P))$  state as mentioned above.

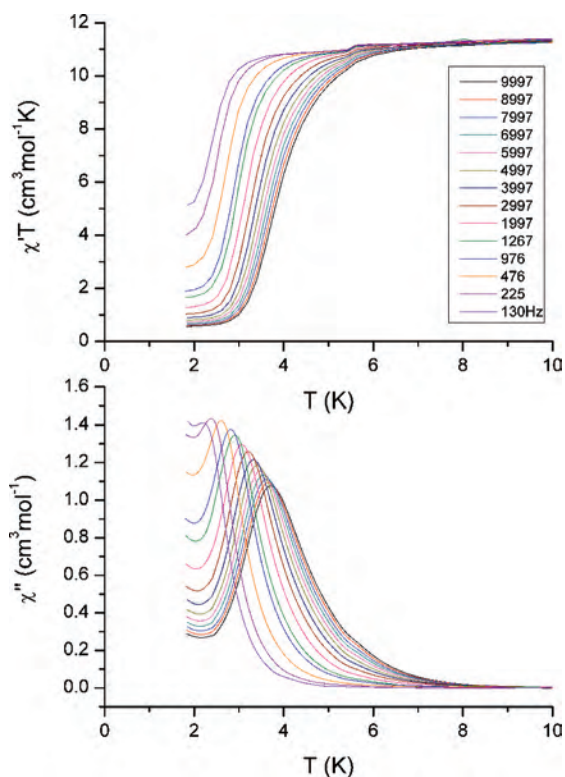
**Magnetic Properties.** The magnetic susceptibility of **1**, measured in a 1 kOe field, is shown in Figure 3. The value of  $\chi T$  at 290 K (11.65 cm $^3$  mol $^{-1}$  K) is consistent with four noninteracting cobalt(II) centers with  $S_i = 3/2$  and  $g = 2.49$ .  $\chi T$  shows a gradual increase to a broad maximum value of 12.7 cm $^3$  mol $^{-1}$  K at 80 K, then decreases with temperature, with a more rapid decline below 10 K. This broad maximum is typical for cobalt(II) compounds and arises from single-ion spin–orbit coupling.<sup>21</sup> The decrease in  $\chi T$  at low temperature is consistent with the presence of intramolecular antiferromagnetic exchange coupling and the sharp drop below 10 K due to zero-field splitting effects. However, due to the large orbital contribution of cobalt(II) it is difficult to perform a quantitative analysis of the susceptibility data. The magnetization curve measured at 2 K is shown in the inset of Figure 3. There is a rapid increase from 0 to 0.7 T, and then the magnetization starts to plateau before increasing again above 2 T ( $M/N\beta = 4.8$  at 2 T). Clearly, the ground

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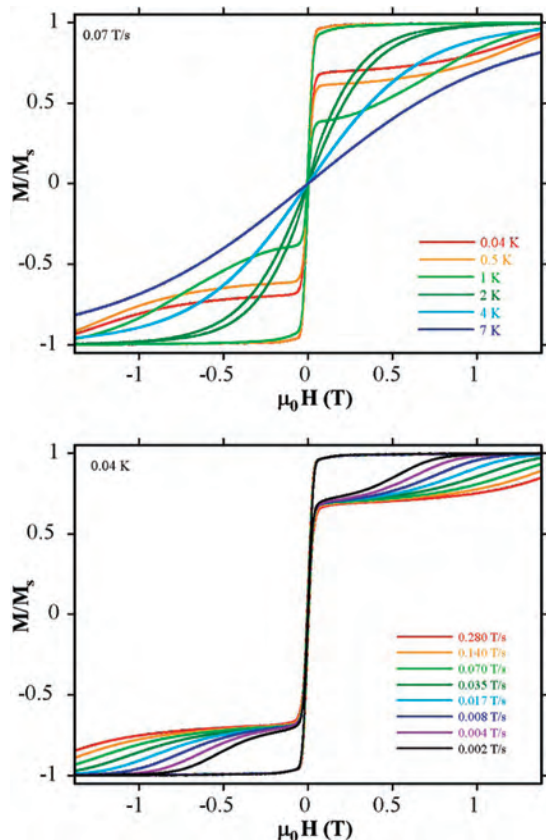
**Figure 3.** Temperature dependence of  $\chi T$  for **1**. Inset shows the field dependence of the magnetization at 2 K.



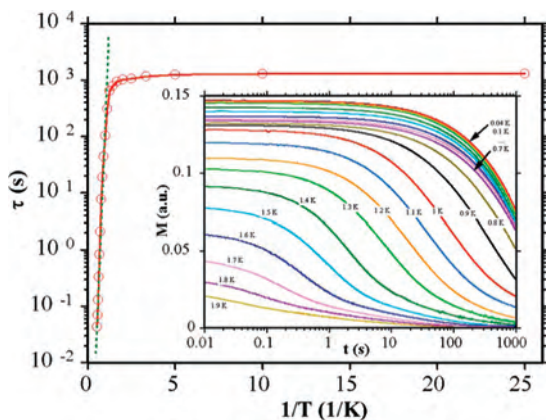
**Figure 4.** The in-phase and out-of-phase components of the ac susceptibility for **1** shown as  $\chi'T$  vs  $T$  (upper) and  $\chi''$  vs  $T$  (lower).

state is magnetic in contrast to the previous report.<sup>18</sup> However, the subsequent rise in the magnetization above 2 T is consistent with the presence of low-lying excited states, in agreement with Hudson et al.<sup>18</sup>

ac susceptibility data measured between 130 and 9997 Hz is shown in Figure 4. Distinct, frequency-dependent peaks are seen in the out-of-phase ( $\chi''$ ) component of the ac susceptibility. The observation of such ac peaks is indicative of slow relaxation and an Arrhenius analysis (Supporting Information) gives an energy barrier  $\Delta E/k_B = 24$  K, and  $\tau_0 = 3.4 \times 10^{-8}$  s for frequencies between 225 and 1267 Hz. At higher frequencies, the plot of  $\ln(\tau)$  versus  $1/T$  shows curvature suggesting a different relaxation pathway as seen



**Figure 5.** Temperature (upper) and sweep rate (lower) dependence of single crystal magnetization versus field hysteresis loops for **1**.



**Figure 6.** Arrhenius plot using single-crystal (dc) data, measured in an applied field of 0.1 T. Inset shows the magnetization measured as a function of time at the indicated temperatures.

for  $\text{Mn}_{12}$  acetate.<sup>22</sup> The SMM behavior of **1** is confirmed by the observation of magnetization versus field hysteresis loops that are temperature and sweep rate dependent (Figure 5). The loops collapse at zero field due to very fast quantum tunneling of the magnetization (QTM) and have almost no coercivity. There is an effective direct relaxation pathway between the ground-state levels, which arises from the strong orbital contribution. It is interesting to note that the SMM  $[\text{Mn}^{\text{III}}_2\text{Dy}^{\text{III}}_2(\text{tmp})_2(\text{O}_2\text{CMe}_3)_4(\text{NO}_3)_4]^{2-}$  containing dysprosium(III), and hence a significant orbital contribution to the magnetic properties has been found to possess similar fast

QTM at zero field.<sup>23</sup> Single-crystal dc relaxation data was measured in an applied field of 0.1 T (Figure 6), to avoid the  $H = 0$  fast-tunneling transition. An Arrhenius analysis yields the parameters  $\Delta E/k_B = 21$  K, and  $\tau_0 = 8 \times 10^{-7}$  s, which are consistent with those obtained from the ac data above.

## Conclusions

The citrate ligand is able to generate metal–oxo cubane structures that are of particular interest for the creation of single-molecule magnets. The discrete cobalt(II) cubane found in  $[\text{C}(\text{NH}_2)_3]_8\{\text{Co}_4(\text{cit})_4\} \cdot 4\text{H}_2\text{O}$  has been shown to exhibit SMM behavior by ac susceptibility measurements

and by temperature and sweep rate dependent magnetization versus field hysteresis loops. The energy barrier to reorientation of the magnetization is 21 K; however, below 1 K the  $\text{Co}_4$  SMM shows fast tunneling at  $H = 0$ . Future studies will include high-frequency EPR and inelastic neutron scattering studies to investigate further the nature of the electronic structure of the  $\text{Co}_4$  SMM.

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**Supporting Information Available:** PXRD, Arrhenius plot for ac data, hysteresis loops at 0.8 and 1.5 K, and method for the determination of extinction coefficients from the KBr discs. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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