

# A Single-Molecule-Magnetic, Cubane-Based, Triangular Co<sub>12</sub> Supercluster\*\*

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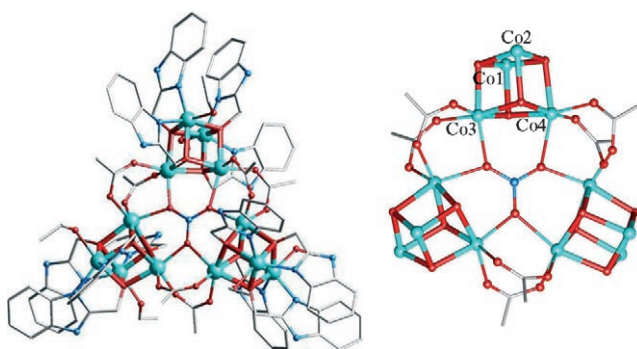
For single-molecule magnet (SMM) behavior, molecular clusters require Ising magnetoanisotropy ( $D_{\text{mol}} < 0$ ) and a large ground-state spin multiplicity.<sup>[1]</sup> These requirements result in a high thermal barrier ( $U$ ) to magnetization relaxation. Such clusters elicit intense interest in both chemistry and physics owing to behavior that is intermediate between that of a simple paramagnet (or classical bulk magnet) and that of a quantum/classical system,<sup>[2]</sup> which heralds applications in quantum devices.<sup>[3]</sup> The development of SMMs is often determined by serendipitous assembly.<sup>[2,4]</sup> However, the synthesis of molecular clusters with SMM-type behaviors presents a formidable challenge because of the difficulties in assembling predetermined structures with predictable magnetic properties.<sup>[4]</sup>

The Mn<sub>12</sub> and Fe<sub>8</sub> clusters and their derivatives<sup>[2,4]</sup> are the most widely studied of homo- and heterometallic SMM systems,<sup>[4–6]</sup> and only very few cobalt-based SMMs are known.<sup>[7]</sup> One reason may be the difficulty in synthesizing cobalt clusters that display a large spin and molecular anisotropy. Because Co<sup>II</sup> has an exceptionally large  $D_{\text{ion}} > 0$  (a characteristic known to dominate molecular anisotropy),<sup>[8]</sup> only a limited number of high-nuclearity clusters are known for cobalt compared with manganese and iron.<sup>[4,7c]</sup>

Previous investigations implied that an alkoxido-bridged metal-cubane structure probably favors ferromagnetic coupling through  $\mu_3$ -O bridges, in which orthogonal hard-axis alignment of four single-ion spins ( $D_{\text{ion}} > 0$ ) may result in a negative  $D_{\text{mol}}$  value for the clusters.<sup>[7a,8]</sup> As 2-(hydroxymethyl)pyridine (hmp) can furnish a cubane-like M<sub>4</sub>O<sub>4</sub> motif,<sup>[9]</sup> we chose the analogous (1*H*-benzimidazol-2-yl)methanol (Hbm) to serve as a chelating/bridging ligand to bring Co<sup>II</sup> ions into cubane-based clusters with carboxylate groups as additional bridging ligands. Herein we report the novel Co<sup>II</sup> cluster

[Co<sub>12</sub>(bm)<sub>12</sub>(NO<sub>3</sub>)(O<sub>2</sub>CMe)<sub>6</sub>(EtOH)<sub>6</sub>](NO<sub>3</sub>)<sub>5</sub> (**1**), which features an unusual Co<sub>12</sub> supercluster and behaves as an SMM.

The crystal structure of **1** reveals a dodecanuclear cluster based on three Co<sub>4</sub>O<sub>4</sub> cubanes bridged by a  $\mu_6$ -nitrate ligand (Figure 1).<sup>[10]</sup> The cubane subunit is constructed by four Co<sup>II</sup> ions and four alkoxido oxygen atoms of  $\mu_3$ - $\eta^1$ : $\eta^3$ -bm ligands.



**Figure 1.** Structures of the cation (left) and Co<sub>12</sub> core (right) of **1**. Co<sup>II</sup> turquoise, O red, N blue, C gray.

The Co1 and Co2 atoms in distorted octahedral N<sub>2</sub>O<sub>4</sub> environments are complexed by two O,N-chelating sites, one bm  $\mu_3$ -alkoxido oxygen atom, and one EtOH ligand. The Co3 and Co4 atoms both form distorted CoO<sub>6</sub> octahedra with three alkoxido groups, two acetate groups, and one nitrate group. The cuboidal core is distorted with all the Co–O–Co angles in the range  $(98 \pm 4)^\circ$  (Table S1 in the Supporting Information) for Co $\cdots$ Co dominant ferromagnetic exchange.<sup>[7a,b]</sup> Similar to the hmp analogue, the Co $\cdots$ Co distances vary from 3.034 to 3.243 Å. A Jahn–Teller distortion of the four d<sup>7</sup> Co<sup>2+</sup> ions lowers the symmetry of the cubes to  $S_4$ . In addition to the central  $\mu_6$ -NO<sub>3</sub><sup>–</sup> bridge, six *syn-syn* acetate ligands also interconnect neighboring cubane units in the supercluster. Five discrete NO<sub>3</sub><sup>–</sup> ions balance the overall positive charge of the cluster. There are no significant intermolecular interactions. A space-filling plot of **1** reveals that the cluster has an approximate trefoil shape with a diameter of about 2.0 nm (Figure S1 in the Supporting Information). High coordination numbers of nitrate, a weak ligand, to transition metal ions were rarely reported,<sup>[11]</sup> and a  $\mu_6$ -nitrate ligand as in **1** (Figure 1) is unprecedented, in contrast to the well-documented  $\mu_6$ -bridging mode of carbonate in metal complexes.<sup>[10,12]</sup> The Co–O(nitrate) bonds are markedly longer than the Ni–O(carbonate) bonds in  $\mu_6$ -carbonate-bridged Ni<sup>II</sup> compounds ((2.111(5) and 2.275(4) Å vs. 2.057–2.076 Å<sup>[10b]</sup>). The Co–O(nitrate)–Co angles ( $99.2^\circ$ ) are also in the range for Co $\cdots$ Co ferromagnetic exchange

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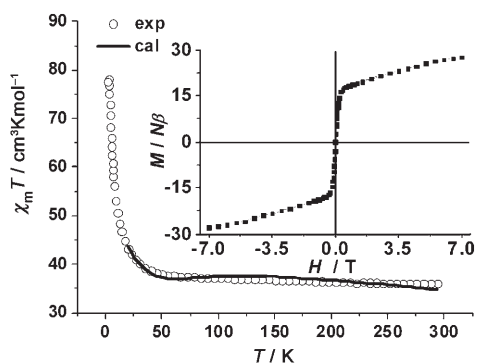
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pathways to be dominant.<sup>[13]</sup> Although  $M_4O_4$  cubanes can act as building blocks for superclusters by vertex sharing, face sharing, or cube capping, the structure of **1** with  $\mu_6$ -nitrate and  $\mu$ -carboxylate bridges appears to be unprecedented.<sup>[4]</sup> Moreover, we could also obtain the structure with  $Ni^{II}$  ions, which emphasizes the coordinative flexibility and versatility of the bm ligand and its synthetic utility in metal cluster chemistry.

The magnetic susceptibility of **1** was measured on a polycrystalline powder sample. The dc magnetic susceptibility ( $\chi_M$ ) measurements in the 2–320 K range at 1000 Oe (Figure 2) showed a  $\chi_M T$  value of  $35.98 \text{ cm}^3 \text{ K mol}^{-1}$  at 295 K, similar to that of a  $Co_{12}$  wheel.<sup>[14]</sup> This value is much



**Figure 2.** Plot of  $\chi_M T$  vs.  $T$  at an applied field of 1000 Oe from 2 to 300 K. Solid line: fitted by the Lines model. Inset:  $M$  vs  $H$  plot at 2 K.

higher than that expected for 12 isolated spin-only  $S_i = 3/2$  ions ( $22.5 \text{ cm}^3 \text{ K mol}^{-1}$  with  $g_{Co} = 2$ ), which is attributed to the orbital contribution of  $Co^{II}$ , which is known to be significant in an octahedral field.<sup>[15]</sup> As  $T$  decreases,  $\chi_M T$  smoothly increases to  $43.19 \text{ cm}^3 \text{ K mol}^{-1}$  at about 20 K, while on further decrease in  $T$ , it rapidly increases to a maximum of  $78.08 \text{ cm}^3 \text{ K mol}^{-1}$  at 2.4 K before eventually falling to  $77.63 \text{ cm}^3 \text{ K mol}^{-1}$  at 2.0 K. The smooth increase in  $\chi_M T$  from 295 to 20 K is generally associated with a compensation of ferromagnetism by the combined effects of spin–orbit coupling of the  $Co^{II}$  ions in **1**.<sup>[16,17]</sup> The increase below 20 K is due to ferromagnetic interactions between the effective spins  $S_i'$  of  $Co^{II}$ . In the low-temperature limit the effective spin  $S_T$  of the molecule may be equal to  $12 \times 1/2 = 6$ .<sup>[14]</sup> We note that this is an oversimplified picture, as the  $S_T$  classification is applicable only in the case of isotropic exchange. The gradual decrease of  $\chi_M T$  below 2 K is best ascribed to the large anisotropy of the  $Co^{II}$  centers.<sup>[7,10b,17]</sup>

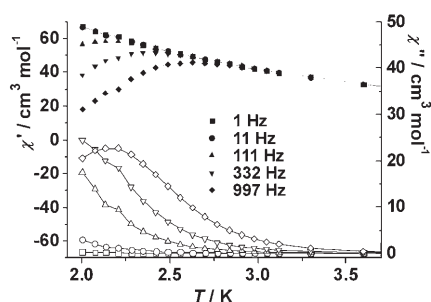
The field dependence of the magnetization increases almost linearly for higher fields than 0.4 T and reaches  $27.8 N\beta$  at 7 T without saturation (Figure 2, inset). Taking  $S_T = 6$ , we obtain  $g = 4.63$ , which is compatible with the average powder  $g$  value observed for  $Co^{II}$  center with effective spin  $S_i' = 1/2$  at low temperature (typically below 30 K).<sup>[16,17]</sup> No divergence between the zero-field-cooled (ZFC) and field-cooled (FC) magnetization, and thus no long-range magnetic ordering of **1** at low temperature (Figure S2 in the Supporting Information), was observed. No magnetic hysteretic behavior could be observed at 2 K.

Zero-field splitting<sup>[18]</sup> and the more common complications arising from spin–orbital interaction<sup>[17,19]</sup> are frequent sources of difficulty in the interpretation of magnetic data for  $Co^{II}$  complexes. As an exact mathematical expression to evaluate the susceptibility of such a complex  $Co_{12}$  system as that of **1** has not been developed, according to Lines theory<sup>[20]</sup> taking into account spin–orbit coupling, we used an admittedly simple model instead. The temperature dependence of  $\chi_M$  for **1** can be attributed to the intra- and intercubane interactions  $J$  and  $J'$ . A least-squares fit of the data above 30 K gave  $J = 5.61 \text{ cm}^{-1}$ ,  $zJ' = 0.37 \text{ cm}^{-1}$ ,  $\lambda = -180 \text{ cm}^{-1}$ ,  $k = 0.57$ , and  $R = 2.02 \times 10^{-4}$  for **1** (Figure 2; Figure S3 in the Supporting Information), indicative of a relatively strong ferromagnetic intracubane  $Co^{II}$  interaction, similar to those observed in several related octahedral  $Co^{II}$  complexes with similar cuboidal cores,<sup>[7a,b,19b]</sup> and weak ferromagnetic intercubane  $Co^{II}$  interactions. The exchange interaction within individual  $Co^{II}$  complexes of **1** is difficult to accurately estimate because of the effects of spin–orbit coupling.

Examination of the bond lengths and angles between the  $Co^{II}$  centers in **1** for magnetostructural correlations reveals an obvious trend, in spite of the wide range of ligands used to construct the cluster. When the values reported for different cobalt(II) clusters are compared, some general observations can be made. Firstly, the intracubane Co–O–Co angles (Table S1), which generally range from  $94.5$  to  $102.1^\circ$ , should favor ferromagnetic interactions because of the significant orbital orthogonality between the metal centers and the bridging atom.<sup>[7a,9,13]</sup> In **1**, the smaller intracubane Co–O–Co angles, together with average Co–O distances that are shorter than the intercubane distances, tend to yield better orthogonality and ferromagnetic  $J$  values larger than the  $J'$  values. On the other hand, there are two *syn-anti* and one *anti-anti* nitrate bridges and two *syn-syn* acetato bridges between two cubes, as opposed to one *syn-syn* nitrate bridge between two intracubane  $Co^{II}$  centers. Usually, the *syn-anti* or *syn-syn, anti-anti* coordination modes for nitrate and carbonate allow weak ferro- or antiferromagnetic coupling.<sup>[12b,15]</sup> This contribution of the compensation of weak coupling (especially the *syn-syn* acetato bridges with short distances of  $3.342 \text{ \AA}$  obviously favor antiferromagnetic coupling)<sup>[15]</sup> diminishes the ferromagnetic exchange more in  $J'$  than in  $J$ . Then the aforementioned effect of the countercomplementarity justifies the greater value for  $J$  than for  $J'$ .

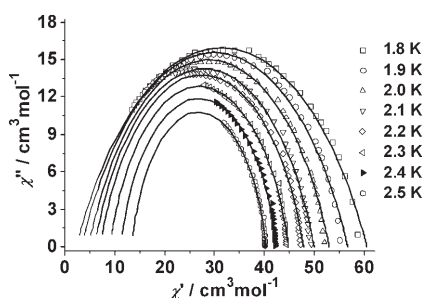
Measuring the ac susceptibility of **1** in the range of 1–997 Hz revealed that it exhibits slow relaxation effects (Figure 3). As the frequency of the oscillating 5-G field increases, a lag in the in-phase component of the molar ac susceptibility  $\chi'$  is observed at low temperatures (top) along with a corresponding rise in the out-of-phase susceptibility  $\chi''$  (bottom) below 3 K, which suggests slow magnetic relaxation. Although a peak occurs for  $\chi''$  at 997 Hz down to 2.2 K, maxima in  $\chi'$  cannot be observed even at the low-temperature (1.8 K) and high-frequency (1200 Hz) limits of our SQUID magnetometer. Therefore, a detailed study of the ac susceptibility was needed.

At fixed temperatures in the range of 1.8–2.5 K (0.1-K steps) around the cusp of the out-of-phase component  $\chi''$ , a series of semicircular portions of Cole–Cole diagrams was



**Figure 3.** Plots of ac susceptibilities  $\chi'$  (full symbols) and  $\chi''$  (open symbols) vs  $T$ .

obtained ( $\chi'$  versus  $\chi''$  plot, Figure 4), which can be fitted by a generalized Debye model<sup>[21]</sup> with an  $\alpha$  parameter of 0.14–0.36 (Table S2 and Eqs. S1, S2), as well as the plots of asymmetric



**Figure 4.** Cole–Cole plots for **1**. Data were collected from 1 to 1200 Hz at 1.8–2.5 K with zero dc field. The solid lines are least-squares fits to a distribution of single relaxation processes with a generalized Debye model.

semicircles complemented by the fitting data, which indicate a moderate distribution of relaxation time, consistent with the wide shape of the ac susceptibility as a function of temperature,<sup>[22]</sup> and further confirming SMM behavior and excluding interpretation as a spin-glass or random-domain magnet.<sup>[21c,d]</sup>

Least-squares fitting of the Arrhenius equation to the obtained magnetization relaxation data gave a good fit with an effective barrier height for magnetization reversal of  $U_{\text{eff}} = 15.0$  K ( $10.4$  cm<sup>−1</sup>) and a preexponential term of  $\tau_0 = 1.94 \times 10^{-7}$  s (the “relaxation-attempt” frequency), which are consistent with values for other SMMs (Figure S4 in the Supporting Information).<sup>[6,7]</sup> It can be concluded on the basis of these data that only one magnetization relaxation process is operative in **1**. Moreover, a distribution is present in this single relaxation process. This could be due to different environments of Co<sub>12</sub> clusters in the crystal resulting from the presence of defects.<sup>[21c]</sup> Such a distribution of cluster environments would lead to a distribution of zero-field-splitting parameters  $D$ , and this affects the potential energy barrier height. A distribution in transverse zero-field interactions could also affect the rate of magnetization quantum tunneling.<sup>[2,18]</sup>

The situation present in **1** is fundamentally different from that encountered in most other SMMs,<sup>[1–6]</sup> as the anisotropy

originates from first-order spin–orbit coupling effects in the single ion.<sup>[17,21]</sup> This is highly anisotropic and characterized by  $S'_i = 1/2$ , a fictitious single-ion spin, at very low temperature. The exchange coupling of 12 of these Kramers doublets produces the splitting pattern, which is responsible for the rise of  $\chi_M T$  below 20 K as well as for the results of the magnetization measurements and consequently also for the SMM behavior of the cluster.<sup>[16,17]</sup> Ising-type ferromagnetic coupling of the 12 Kramers doublets leads to a  $M_S = \pm 6$  ground state with numerous  $|MS' < 6|$  cluster states lying within 20 K. This ordering of levels creates the energy barrier necessary for SMM behavior.

Analysis of the field dependence of magnetization from 0.5–7 and 0.1–0.8 T between 1.8 and 4.0 K yielded results that point to population of low-lying excited states due to a small  $J'$  value.<sup>[23]</sup> The treatment of reduced magnetization was further complicated by the magnetic anisotropy of the Co<sup>II</sup> ions, which prevents saturation of **1** in weak fields (Figure S5 in the Supporting Information).<sup>[6c]</sup> Ultimately, high-field EPR experiments will be needed to obtain accurate values for  $g$  and zero-field-splitting parameters. Despite the difficulties inherent in the analysis of this highly anisotropic system, the feasibility of preparing novel high-spin clusters that exhibit SMM behavior from Co<sup>II</sup> ions has been illustrated by the preparation and characterization of **1**. Nonetheless, **1** represents a new example that illustrates how molecular anisotropy occurs when only limited easy-axis ions of single-ion anisotropy are assembled.<sup>[8]</sup> Further theoretical analyses are needed to evaluate the effects of magnetic exchange anisotropy, and further studies at lower temperatures and higher frequencies are planned, as well as investigation of possible hysteresis and quantum tunneling of magnetization.

In summary, **1** is structurally rather unusual and is a rare example of 3d-metal clusters with O and N ligation, which exhibits an interesting SMM behavior and highlights the potential for creating improved SMMs by using Co<sup>II</sup> ions as metal centers. Our results further support the idea that judiciously assembling “super-clusters” with anisotropic shapes from other [M<sub>4</sub>O<sub>4</sub>] cubanes as building blocks may result in magnetic relaxation effects at higher temperatures than that observed for **1** and allow us to probe the effects on SMM behavior of linking two or more clusters.

## Experimental Section

Compound **1** was synthesized from Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (1 mmol), Co(O<sub>2</sub>CMe)<sub>2</sub>·4H<sub>2</sub>O (0.5 mmol), Hbm (0.5 mmol), and triethylamine (0.1 mL) in ethanol (10 mL). The reactants were sealed in a 15-mL teflon-lined, stainless-steel Parr bomb. The bomb was heated at 140 °C for 3 d. The cool solution yielded red block single crystals in ca. 30% yield.

Crystal data of **1**: Trigonal,  $R\bar{3}$  (no. 148);  $a = 18.807(1)$ ,  $c = 75.152(4)$  Å,  $V = 23020(1)$  Å<sup>3</sup>,  $Z = 6$ ,  $\rho_{\text{calcd}} = 1.488$  g cm<sup>−3</sup>,  $\mu = 1.35$  mm<sup>−1</sup>, final  $R_1 = 0.0809$  for  $I \geq 2\sigma(I)$ ,  $wR_2 = 0.2309$  for all data. The intensity data were recorded on a Bruker SMART Apex CCD system with MoK $\alpha$  radiation ( $\lambda = 0.71073$  Å) at 100(2) K. The structure was solved by direct methods and refined by full-matrix least-squares techniques on  $F^2$  by using SHELXTL. CCDC-615488 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge

Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif)

Magnetic susceptibility measurements on **1** were performed with a Quantum Design MPMS-XL7 SQUID. Data were corrected for the diamagnetic contribution calculated from Pascal constants.

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