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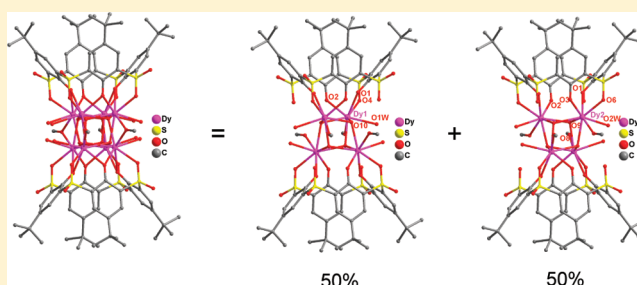
Syntheses, Crystal Structures, and Magnetic Properties of Two *p*-tert-Butylsulfonylcalix[4]arene Supported Cluster Complexes with a Totally Disordered $\text{Ln}_4(\text{OH})_4$ Cubane Core

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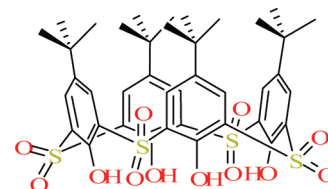
ABSTRACT: Two new sandwich calix[4]arene-supported cluster complexes, $[\text{Ln}_4(\text{OH})_4(\text{TBSOC})_2(\text{H}_2\text{O})_4(\text{CH}_3\text{OH})_4] \cdot 4\text{H}_2\text{O}$ (H_4TBSOC = *p*-tert-butylsulfonylcalix[4]arene; Ln = Dy, 1; Ln = Ho, 2), have been prepared and characterized. An X-ray crystallographic study reveals that both complexes contain a holistically disordered $[\text{Ln}_4(\text{OH})_4]^{8+}$ cubane cluster core, which is sandwiched between two antiparallel calixarene macrocycles. Magnetic investigations indicate that complex 1 displays slow magnetization relaxation typical for single-molecule magnets in the absence of a static applied dc field, with the $\Delta E/k_B$ parameter of 22.9 K, the largest value for the calixarene-supported pure 4f single-molecule magnets so far, whereas complex 2 does not show any relaxation of the magnetization above 2 K.



■ INTRODUCTION

The single-molecule magnets (SMMs), which are characterized as slow magnetization relaxation induced by high spin ground states and uniaxial Ising-like magnetic anisotropy, have attracted significant interest since 1993 owing to their potential applications in such fields as quantum computing, magnetic information storage, and nanoelectronics.¹ The heavier lanthanides, in particular, the Dy(III) ion, are very nice components of SMMs because of their spin variety and large magnetic anisotropy. Recently, a great deal of endeavors have been dedicated to 4f² or 3d-4f³ clusters. Nevertheless, exploring SMMs with a high blocking temperature, T_B , is still a great challenge. On the other hand, calix[4]arenes (C4s) in a cone conformation have been exploited in the construction of various nanoscale polynuclear architectures due to their polyphenolic oxygen atoms being excellent multidentate coordination sites for metal ions.⁴ In particular, some $[\text{Mn}^{\text{III}}_2\text{Mn}^{\text{II}}_2]^{5a-c}$ and $[\text{Mn}^{\text{III}}_4\text{Ln}^{\text{III}}_4]^{5d}$ polynuclear metal clusters supported by *p*-tert-Bu-calix[4]arene were observed to behave as SMMs, and the thia-bridged calix[4]arene analogue *p*-phenylthiacalix[4]arene was also employed in the assembly of a Dy₄ cluster exhibiting slow magnetic relaxation behavior of SMM under a static applied dc field of 1 kOe.⁶

With respect to our interests in polynuclear cluster complexes with interesting magnetic properties,⁷ we are currently focusing on compounds supported by the sulfonyl-bridged calix[4]arene *p*-tert-butylsulfonylcalix[4]arene⁸ (H_4TBSOC , Scheme 1), which possesses excess coordination sites from the sulfonyl O atoms. This multidentate macrocycle ligand has been utilized to construct several lanthanide

Scheme 1. The H_4TBSOC Ligand

metallamacrocycles,^{4f,g} two lanthanide cubane cluster complexes by Yamashita's group,⁹ and a novel nestlike $[\text{Co}_{24}]$ metallamacrocycle by our group.¹⁰ Herein we report a new TBSOC^{4-} supported $[\text{Dy}_4]$ sandwich cluster complex showing the SMM behavior in the absence of a dc field, $[\text{Dy}_4(\text{OH})_4(\text{TBSOC})_2(\text{H}_2\text{O})_4(\text{CH}_3\text{OH})_4] \cdot 4\text{H}_2\text{O}$ (1), which features a disordered $[\text{Dy}_4(\text{OH})_4]^{8+}$ cubane cluster core sandwiched by two TBSOC^{4-} macrocycles. We also obtained its Ho^{3+} analogue $[\text{Ho}_4(\text{OH})_4(\text{TBSOC})_2(\text{H}_2\text{O})_4(\text{CH}_3\text{OH})_4] \cdot 4\text{H}_2\text{O}$ (2), but 2 does not exhibit any magnetization relaxation behavior above 2 K.

■ EXPERIMENTAL SECTION

Materials and Characterization Techniques. All commercial chemicals were used as received without further purification. H_4TBSOC was purchased from TCI (ShangHai) Development Co., Ltd. The elemental analyses were performed on a Varlo ELIII

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elemental analyzer. The infrared spectra were recorded on a BRUKER-TENSOR-27 spectrophotometer with pressed KBr pellets. Variable-temperature magnetic susceptibility, zero-field ac magnetic susceptibility, and field dependence of magnetization were measured on a Quantum Design MPMSXL5 (SQUID) magnetometer. Diamagnetic corrections were estimated from Pascal's constants for all constituent atoms.

Preparation of $[\text{Dy}_4(\text{OH})_4(\text{TBSOC})_2(\text{H}_2\text{O})_4(\text{CH}_3\text{OH})_4]\cdot 4\text{H}_2\text{O}$ (1). A mixture of H_4TBSOC (0.5 mmol), $\text{Dy}(\text{OAc})_3$ (1.0 mmol), and (1*R*,3*S*)-(+)-camphoric acid (0.5 mmol) in 30 mL of $\text{MeOH}/\text{CHCl}_3$ (v/v 2:1) was stirred for 10 min at room temperature. 1.0 mmol of Et_3N was then added, and the solution was stirred for another 24 h at room temperature; the resultant light-yellow solution was evaporated for 1–2 weeks to produce light-yellow needle crystals of **1** (yield 55–60% based on Dy). Anal. Calcd for $\text{C}_{84}\text{H}_{124}\text{Dy}_4\text{O}_{40}\text{S}_8$: C, 37.64; H, 4.66%; Found: C, 37.60; H, 4.69%. IR (KBr, cm^{-1}): 3494(s), 2961(m), 2874(w), 1711(w), 1606(m), 1571(m), 1499(s), 1363(w), 1267(m), 1217(w), 1156(w), 1131(w), 1080(m), 906(w), 838(w), 798(m), 645(w), 620(w), 555(m), 488(w).

Preparation of $[\text{Ho}_4(\text{OH})_4(\text{TBSOC})_2(\text{H}_2\text{O})_4(\text{CH}_3\text{OH})_4]\cdot 4\text{H}_2\text{O}$ (2). Complex **2** was prepared in a procedure similar to that of **1**, except that $\text{Ho}(\text{OAc})_3$ was utilized instead of $\text{Dy}(\text{OAc})_3$. Yield: 50–55%. Anal. Calcd for $\text{C}_{84}\text{H}_{124}\text{Ho}_4\text{O}_{40}\text{S}_8$: C, 37.50; H, 4.65%; Found: C, 37.53; H, 4.69%. IR (KBr, cm^{-1}): 3497(s), 2961(m), 2873(w), 1714(w), 1606(m), 1575(m), 1500(s), 1364(w), 1266(m), 1217(w), 1156(w), 1131(w), 1080(m), 906(w), 838(w), 797(m), 645(w), 619(w), 554(m), 487(w).

X-ray Crystallography. Data were collected at 173(2) K on a Rigaku Saturn 724+ CCD diffractometer with Mo- $\text{K}\alpha$ radiation ($\lambda = 0.71073$ Å). The absorption correction was numerical for the dataset of complex **1**, while was empirical for that of **2**. Cell parameters were obtained by the global refinement of the positions of all collected reflections for two complexes. The structure was solved by direct methods and refined by a full matrix least-squares technique based on F^2 using SHELXL 97 program. All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms but those in water molecules, alkoxide groups, and hydroxo anions were refined as riding atoms. Disorder was observed in four Ln atoms with the same occupancy factor of 0.5 in both **1** and **2**. Besides, there are three disordered *p*-tert-butyl groups in each TBSOC^{4-} ligand of two complexes. Notably, the disorder of solvent hydrate molecules could reduce the quality of crystal structures markedly, so the SQUEEZE routine in PLATON¹¹ was applied to give better refinement. Selected crystallographic data and structure determination parameters for complexes **1** and **2** are given in Table 1. CCDC reference numbers: CCDC 833580 and 833581.

RESULTS AND DISCUSSION

Preparation. The reaction of H_4TBSOC , $\text{Ln}(\text{OAc})_3$, and (1*R*,3*S*)-(+)-camphoric acid (1:2:1) in a $\text{MeOH}/\text{CHCl}_3$ (v/v 2:1) mixed solvent in the presence of triethylamine (1 equiv) produces **1** (Ln = Dy) or **2** (Ln = Ho) in good yields. (1*R*,3*S*)-(+)-camphoric acid is necessary for the reactions although it is not incorporated into the structures of **1** and **2**. Absence of (1*R*,3*S*)-(+)-camphoric acid would result in noncrystalline materials, and attempts to use other organic bis-carboxyl acids such as malonic acid, succinic acid, and glutaric acid instead of (1*R*,3*S*)-(+)-camphoric acid failed. A similar trend was also observed by our group when a ringlike octadecanuclear mixed-valence manganese cluster complex, $[\text{Mn}^{\text{II}}_8\text{Mn}^{\text{III}}_6\text{Mn}^{\text{IV}}_4(\text{OH})_4\text{O}_2(\text{acac})_6(\text{thmp})_{12}]\cdot 5\text{H}_2\text{O}$ (Hacac = acetylacetone, $\text{H}_3\text{thme} = 1,1,1$ -tris-(hydroxymethyl)-propane), was synthesized recently,^{7d} in which (*R*-, *S*-, or racemic) 2-aminopropane-1,2-diol played a similar boost role. For comparison, another two TBSOC^{4-} -supported cluster complexes $(n\text{Bu}_4\text{N})_4[\text{Ln}_4(\text{TBSOC})_2(\text{OH})_4(\text{AcO})_4]$ (Ln = Eu or Tb),⁹ which also contain a $[\text{Ln}(\text{OH})_4]^{8+}$ cubane cluster core

Table 1. Crystal Data and Structural Refinement Parameters for **1** and **2**

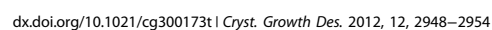
	1	2
chemical formula	$\text{C}_{84}\text{H}_{124}\text{Dy}_4\text{O}_{40}\text{S}_8$	$\text{C}_{84}\text{H}_{124}\text{Ho}_4\text{O}_{40}\text{S}_8$
formula weight	2680.38	2690.10
crystal system	orthorhombic	orthorhombic
space group	<i>Pnmm</i>	<i>Pnmm</i>
<i>a</i> (Å)	32.308(6)	32.268(6)
<i>b</i> (Å)	12.271(2)	12.356(2)
<i>c</i> (Å)	20.700(4)	20.790(4)
<i>V</i> /Å ³	8207(3)	8289(3)
<i>Z</i>	2	2
<i>T</i> (K)	173 (2)	173 (2)
$\lambda(\text{Mo}-\text{K}\alpha)$ (Å)	0.71073	0.71073
$\rho_{\text{calc}}/\text{g}\cdot\text{cm}^{-3}$	1.049	1.043
$\mu(\text{Mo}-\text{K}\alpha)/\text{mm}^{-1}$	1.951	2.038
θ range (°)	$1.17 \leq \theta \leq 26.60$	$2.02 \leq \theta \leq 25.02$
limiting indices	$-26 \leq h \leq 40, -14 \leq k \leq 14, -19 \leq l \leq 26$	$-26 \leq h \leq 38, -10 \leq k \leq 14, -14 \leq l \leq 24$
reflections collected	28106	23256
unique reflections	8575	7512
R_1^a [$I > 2\sigma(I)$]	0.0658	0.0594
wR_2^b [$I > 2\sigma(I)$]	0.1811	0.1718
R_1^a [all data]	0.0823	0.0688
wR_2^b [all data]	0.1899	0.1779
goodness-of-fit on F_o^2	1.011	1.059

$$^a R_1 = \sum |F_o| - |F_c| / \sum |F_o|, \quad ^b wR_2 = \sum \{ [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}.$$

but the whole molecules are composed of both the cation and anion parts, were prepared by reaction of dinuclear complex precursor $(n\text{Bu}_4\text{N})_2[\text{Ln}_2(\text{TBSOC})_2(\text{H}_2\text{O})_4]$ (Ln = Eu or Tb) with $\text{Ln}(\text{AcO})_3 \cdot n\text{H}_2\text{O}$ and $n\text{Bu}_4\text{NOH}$ recently. It is noteworthy that not any magnetic properties of $(n\text{Bu}_4\text{N})_4[\text{Ln}_4(\text{TBSOC})_2(\text{OH})_4(\text{AcO})_4]$ had been reported.⁹

Crystal Structures of **1 and **2**.** Complexes **1** and **2** have similar structures, so **1** is employed as a representation to be described in detail. Analysis of single-crystal X-ray diffraction data collected at 173 K revealed that complex **1**, which crystallizes in the orthorhombic space group *Pnmm*, possesses a sandwich structure composed of one disordered $[\text{Dy}_4(\text{OH})_4]^{8+}$ cubane cluster core cation, two tail-to-tail TBSOC^{4-} anions, four terminal methanol molecules, and four terminal hydrate molecules (Figure 1). In addition, there are some solvent hydrate molecules in the crystal lattice. Surprisingly, all four Dy atoms have been presumed in disordered sites with the same occupancy factor of 0.5. Such a disorder maintained at a low-temperature (173 K) suggests that it belongs to the positional-disorder.¹²

In Figure 1a, the TBSOC^{4-} ligand seems to bridge four Dy atoms using its four η^2 -phenoxy O atoms, generating an isosceles trapezoid Dy_4 cluster with the $\text{Dy}\cdots\text{Dy}$ lengths of 2.578, 2.637, 2.637, and 2.735 Å; however, these distances are quite smaller than those in the solvothermally synthesized thiacalix[4]arene-supported planar Dy_4 clusters, $[\text{Dy}^{\text{III}}_4(\text{PTC4A}/\text{TC4A})_2(\mu_4\text{-OH})\text{Cl}_3(\text{CH}_3\text{OH})_2(\text{H}_2\text{O})_3]$



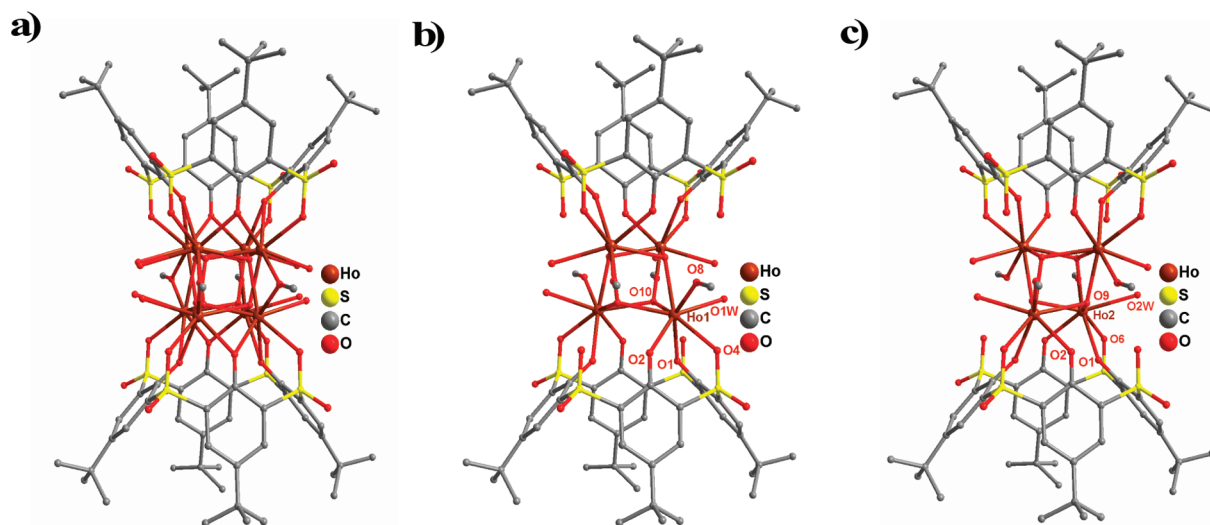


Figure 2. Crystal structure of **2**. All Ho atoms and all coordination hydrate molecules have an occupancy factor of 0.5 (a). Comparison of the closely similar configurations of the two species present in the lattice (b and c).

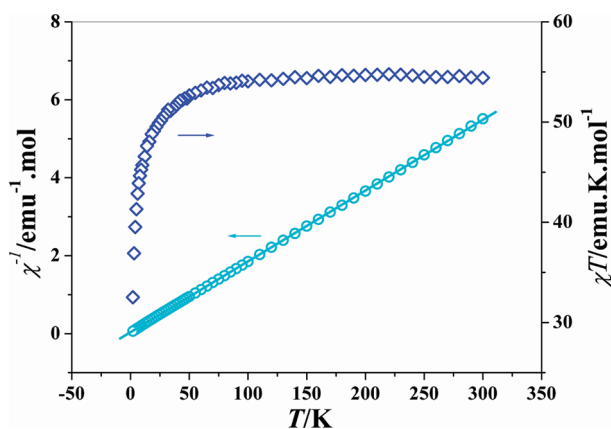


Figure 3. Plots of $\chi_M T$ and χ_M^{-1} versus T of **1**. The solid line represents the best theoretical fitting.

$\times 10^{-8}$ s and $\Delta E/k_B = 22.9$ K (Figure 5a), suggesting a thermally activated mechanism. The $\Delta E/k_B$ value of **1** (22.9 K) is comparable with those of $[\text{Mn}^{\text{III}}_2\text{Mn}^{\text{II}}_2]$ SMMs^{5a-c} (≤ 23.7 K) but obviously larger than those of $[\text{Mn}^{\text{III}}_4\text{Ln}^{\text{III}}_4]$ SMMs^{5d}

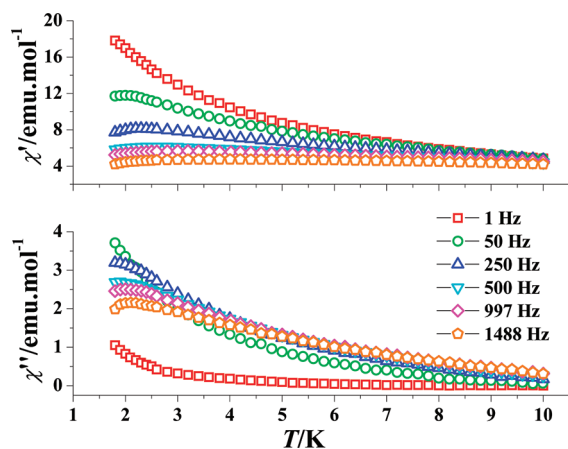


Figure 4. The ac susceptibilities of **1** measured in $H_{ac} = 2.5$ Oe and $H_{dc} = 0$.

supported by *p*-*tert*-Bu-calix[4]arene (≤ 5 K). As expected for a Debye model with a single relaxation time (τ), two semicircle Cole–Cole diagrams were obtained at 1.9 and 2.5 K, respectively (Figure 5b).¹⁵ The best fitting gives the α parameter of 0.48 and 0.47 for 1.9 and 2.5 K, respectively, indicating a distribution in this single relaxation process.^{15c} Additionally, the shift of peak temperature (T_f) of χ'' is evaluated with a parameter $\phi = (\Delta T_f/T_f)/\Delta(\log f) = 0.17$; this value is a normal value for a superparamagnet ($0.1 < \phi < 0.3$), precluding any possibility of the spin glass state ($\phi \approx 0.01$). Moreover, the M versus H plot of **1** exhibits no hysteresis at 1.9 K (Figure 6).

Tang group's recent investigations indicated that the Dy–O_{hydroxy}–Dy angle in the $[\text{Dy}_4(\text{OH})_4]^{8+}$ cubane has a great influence on the SMM properties: the SMM behavior only appears when this angle is larger than 99° .¹⁶ The Dy–O_{hydroxy}–Dy cubane angles in complex **1** range from $106.1(4)$ to $107.9(3)^\circ$ (Table 2), which are obviously larger than 99° , so the SMM properties of **1** are expected. Up to now, only a few pure 4f SMMs supported by calixarene ligands have been reported. For example, two thiocalix[4]arene-supported planar Dy₄ clusters, $[\text{Dy}^{\text{III}}_4(\text{PTC4A}/\text{TC4A})_2(\mu_4\text{-OH})\text{-Cl}_3(\text{CH}_3\text{OH})_2(\text{H}_2\text{O})_3]$, also display slow magnetic relaxation behavior.⁶ However, their semicircle Cole–Cole diagrams were not observed, and the estimation of τ_0 and ΔE parameters failed utilizing the Arrhenius law because the slow relaxation of magnetization was obtained only over a short-range of temperature and frequency.⁶ A similar case was also found in the TBSOC⁴⁻ supported dinuclear terbium(III) complex $[\text{Tb}^{\text{III}}_2(\text{TBSOC})_2(\text{NO}_3)_2(\text{dmf})_6]\cdot 2\text{dmf}$.^{14b} It is noteworthy that the complexes $[\text{Dy}^{\text{III}}_4(\text{PTC4A}/\text{TC4A})_2(\mu_4\text{-OH})\text{-Cl}_3(\text{CH}_3\text{OH})_2(\text{H}_2\text{O})_3]$ ⁶ and $[\text{Tb}^{\text{III}}_2(\text{TBSOC})_2(\text{NO}_3)_2(\text{dmf})_6]\cdot 2\text{dmf}$ ^{14b} require the application of an external dc field to display slow relaxation behavior, while complex **1** displays slow magnetic relaxation behavior in the absence of a dc field. Complex **1** possesses the highest energy barrier for the calixarene-supported 4f SMMs so far. Besides the aforementioned lanthanide ions,¹³ other types of heavy metal atoms showing the positional-disorder remain scarce in molecule systems, they possess no magnetic properties, or their magnetic properties were not reported.¹⁷ To the best of our knowledge,

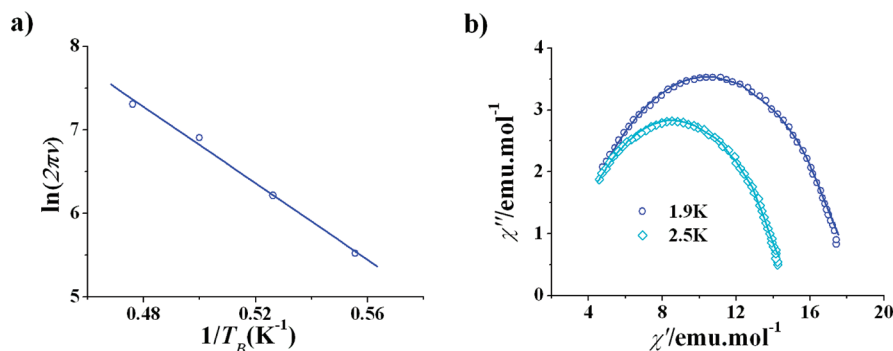


Figure 5. Plot of $\ln(2\pi\nu)$ vs $1/T_B$ of **1**; the solid line represents the best fitting by Arrhenius law (a). Cole–Cole diagrams of **1** at 1.9 and 2.5 K, respectively; the solid lines represent the best theoretical fitting (b).

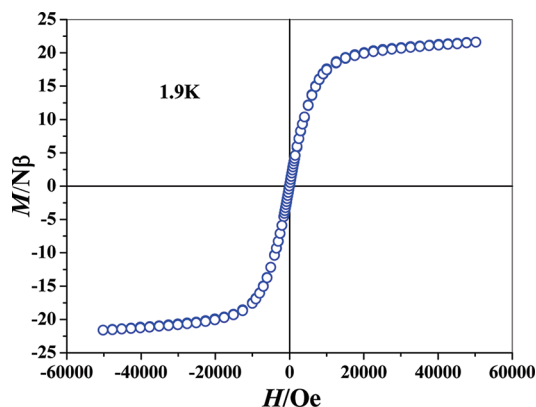


Figure 6. Hysteresis loop at 1.9 K for **1**.

complex **1** is the first SMM containing a totally disordered metal cluster core.

The $\chi_M T$ value at room temperature of **2** is 53.15 emu·K·mol^{−1} (Figure 7), which is slightly lower than the

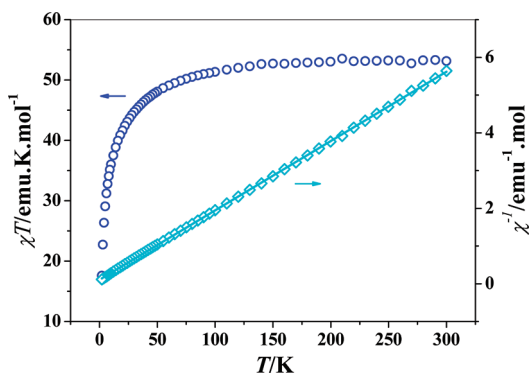


Figure 7. Plots of $\chi_M T$ and χ_M^{-1} versus T of **2**. The solid line represents the best theoretical fitting.

theory value of four noninteracting Ho³⁺ ions in the ⁵I₈ ground state (56.24 emu·K·mol^{−1}, $S = 2$, $L = 6$, $g = 5/4$). Similar to **1**, a steady decrease of the $\chi_M T$ values is observed with decreasing temperature down to 50 K. At lower temperatures, the $\chi_M T$ values decrease dramatically to 17.59 emu·K·mol^{−1} at 2 K. The susceptibility data ranging from 2 to 300 K were fitted to the Curie–Weiss law, leading to $C = 54.38$ cm³ mol^{−1} K and $\theta = -5.73$ K. Unlike **1**, ac susceptibility investigations of **2** showed that no out-of-phase signal (χ_{ac}'') was found in the region of 2–10 K under a 2.5 Oe oscillating field at frequencies from 1 Hz

up to 1488 Hz (Figure 8). No slow paramagnetic relaxation observed above 2 K for **2** could be ascribed to the spin parity effect.¹⁸

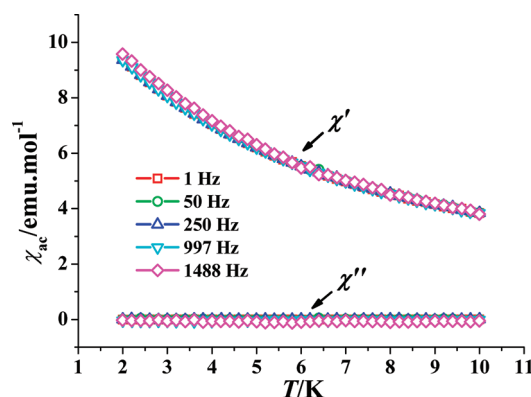


Figure 8. The ac susceptibilities of **2** measured in $H_{ac} = 2.5$ Oe and $H_{dc} = 0$.

CONCLUSIONS

In summary, in the presence of (1*R*,3*S*)-(+)-camphoric acid, we have successfully prepared a TBSOC^{4−} supported Dy₄ cluster complex showing the SMM behavior, whose energy barrier is the highest for the calixarene-supported 4f SMMs to date, and the [Dy₄(OH)₄]⁸⁺ cubane cluster core is wholly disordered. Complex **1** represents the first SMM with a holistically disordered metal cluster core. Furthermore, its Ho³⁺ analogue was also isolated, but no magnetization relaxation behavior observed above 2 K. This work demonstrates that the TBSOC^{4−} ligand can be used to prepare SMMs, and the positional-disorder of several heavier lanthanide atoms can happen synchronously in a suitable molecule material system.

ASSOCIATED CONTENT

Supporting Information

Crystallographic information files. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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