

Supporting Information

Slow Magnetic Relaxation in a Dysprosium Ammonia Metallocene Complex

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Additional Experimental Details

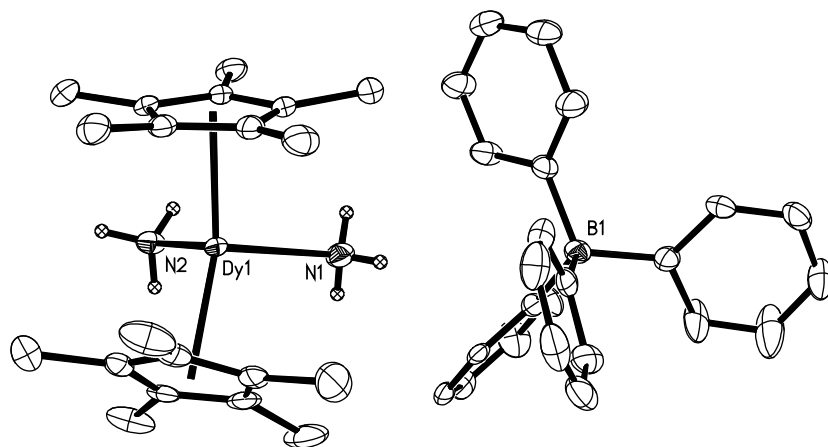


Figure S1: Thermal ellipsoid plot of $[(C_5Me_5)_2Dy(NH_3)_2][BPh_4]$, **1**. All hydrogen atoms except those belonging to the NH_3 ligands have been omitted for clarity. Selected bond lengths (Å) and angles (°) (Cnt = C_5Me_5 ring centroid): Dy–Cnt_{ave}, 2.350; Dy–N1, 2.476(3); Dy–N2, 2.466(3); N1–Dy–N2, 89.03(11); Cnt1–Dy–Cnt2, 140.2.

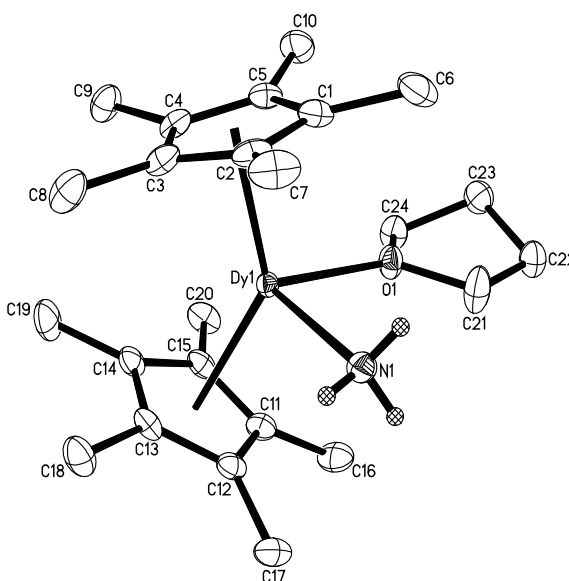
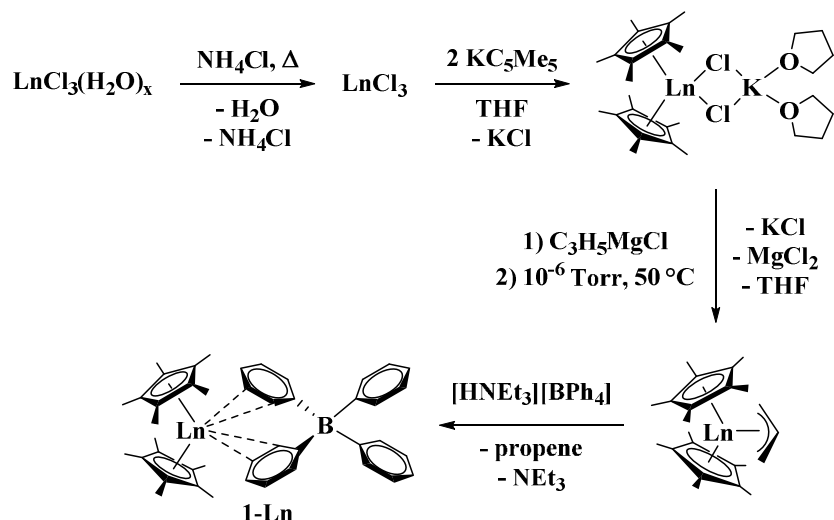


Figure S2. Thermal ellipsoid plot of $[(C_5Me_5)_2Dy(NH_3)(THF)][BPh_4]$, **2**, drawn at the 50% probability level. Hydrogen atoms, except those on NH_3 , and counter anion $[BPh_4]^{1-}$ are omitted for clarity. Selected bond lengths (Å) and angles (°): Dy–Cnt_{ave} (Cnt = C_5Me_5 ring centroid), 2.370; Dy–O, 2.370(2); Dy–N, 2.486(2); Cnt–Dy–Cnt, 139.2; N–Dy–O, 91.50(7).



Scheme S1. Established synthetic scheme for the unsolvated metallocene cationic complexes $[(\text{C}_5\text{Me}_5)_2\text{Ln}][(\mu\text{-Ph})_2\text{BPh}_2]$ ($\text{Ln} = \text{Y}$, lanthanides) that first led to unexpected isolation of **1**.

$(\text{C}_5\text{Me}_5)_2\text{DyCl}_2\text{K}(\text{THF})_2$. Synthesized as previously reported.^{1,2} In a nitrogen-filled glovebox, KC_5Me_5 (2.9 g, 17 mmol) was added over 20 min to a stirring slurry of DyCl_3 (2.4 g, 8.8 mmol) in THF (15 mL) to yield an opaque mixture. After stirring 2 d, the reaction mixture was centrifuged to remove white solids. The pale yellow supernatant was filtered and the solvent was removed from the filtrate under reduced pressure to yield a yellow solid that was washed with toluene and hexane and dried to produce $(\text{C}_5\text{Me}_5)_2\text{DyCl}_2\text{K}(\text{THF})_2$ as an off-white solid (3.2 g, 62% yield).

$(\text{C}_5\text{Me}_5)_2\text{Dy}(\text{C}_3\text{H}_5)$. Synthesized as previously reported.^{1,2} Addition of a solution of $(\text{C}_3\text{H}_5)\text{MgCl}$ in THF (2.7 mL, 5.2 mmol) to a pale yellow solution of $(\text{C}_5\text{Me}_5)_2\text{DyCl}_2\text{K}(\text{THF})_2$ (3.2 g, 5.2 mmol) in toluene (175 mL) caused an immediate color change to bright yellow. After the mixture was stirred overnight, the solvent was removed under reduced pressure to yield a tacky yellow-orange solid. Treatment with 10:1 hexane/dioxane overnight generated a white precipitate that was separated by centrifugation. Removal of solvent from the yellow supernatant gave $(\text{C}_5\text{Me}_5)_2\text{Dy}(\text{C}_3\text{H}_5)(\text{THF})_x$ as a yellow-orange solid which was transferred to a sublimation tube equipped with a sealable Teflon adapter and desolvated by exposure to vacuum (1×10^{-6} Torr at 50°C) for 5 d. The apparatus was brought into a nitrogen-filled glovebox free of coordinating solvents. Extraction into hexanes and removal of solvent under reduced pressure provided $(\text{C}_5\text{Me}_5)_2\text{Dy}(\text{C}_3\text{H}_5)$ (1.53 g, 62% yield) as a bright orange solid. Crystals of $(\text{C}_5\text{Me}_5)_2\text{Dy}(\text{C}_3\text{H}_5)$ were grown from hexane at -30°C .

$[(\text{C}_5\text{Me}_5)_2\text{Dy}][(\mu\text{-Ph})_2\text{BPh}_2]$. As previously reported,² addition of $(\text{C}_5\text{Me}_5)_2\text{Dy}(\text{C}_3\text{H}_5)$ (1.2 g, 2.6 mmol) to a slurry of $[\text{HNEt}_3][\text{BPh}_4]$ (1.04 g, 2.5 mmol) in toluene (15 mL)

produced a cloudy orange mixture that was stirred overnight. The mixture was filtered and the collected solids were washed sequentially with toluene and hexane and dried to yield a pale yellow solid (1.82 g, 98% of $[(C_5Me_5)_2Dy][(\mu-Ph)_2BPh_2]$).

Initial Synthesis of $[(C_5Me_5)_2Dy(NH_3)_2][BPh_4]$, 1. Recrystallization of yellow solid from the synthesis of $[(C_5Me_5)_2Dy][(\mu-Ph)_2BPh_2]$ described above from hot toluene yielded colorless crystals identified by X-ray crystallography to be $[(C_5Me_5)_2Dy(NH_3)_2][BPh_4]$, 1. Attempts to reproduce this result using a different batch of intermediates starting with the same $DyCl_3$ source only yielded pale yellow crystals of the known unsolvated cation $[(C_5Me_5)_2Dy][(\mu-Ph)_2BPh_2]$.^{2,3}

$(C_5Me_5)_2Dy(C_3H_5)_2(THF)$. In an attempt to understand how the bis(ammonia) product $[(C_5Me_5)_2Dy(NH_3)_2][BPh_4]$, 1, had formed, the allyl precursor $(C_5Me_5)_2Dy(C_3H_5)(THF)$, was remade from the same $DyCl_3$ batch as described above. However, crystallization this time from cold hexane before desolvation under vacuum yielded a mixture of yellow and orange crystals. X-ray crystallography identified the yellow crystals as the bis(allyl) THF solvate $(C_5Me_5)_2Dy(C_3H_5)_2(THF)$ (Figure S3), and the orange crystals as the known mono(allyl) unsolvated species $(C_5Me_5)_2Dy(C_3H_5)$. Subsequent attempts to isolate crystals of the bis(allyl) product under various conditions only yielded the known mono(allyl) complex $(C_5Me_5)_2Dy(C_3H_5)$. For example, reactions of $(C_5Me_5)_2DyCl_2K(THF)_2$ with two equiv of $(C_3H_5)MgCl$ gave only crystals of $(C_5Me_5)_2Dy(C_3H_5)(THF)$. Ligand redistribution is common in the chemistry of lanthanide complexes of small cyclopentadienyl ligands,⁴ but it is not common in pentamethylcyclopentadienyl systems since $(C_5Me_5)_3Dy^3$ is so sterically crowded that it is not a viable ligand redistribution product. Attempts to make the bis(allyl) product by addition of excess $(C_3H_5)MgCl$ to $(C_5Me_5)_2Dy(C_3H_5)$ were unsuccessful. Evidently, under some crystallization conditions, the bis(allyl) product can be isolated as a minor product even when $(C_5Me_5)_2Dy(C_3H_5)(THF)$ is the main product and the only product isolated from further recrystallizations of the same batch.

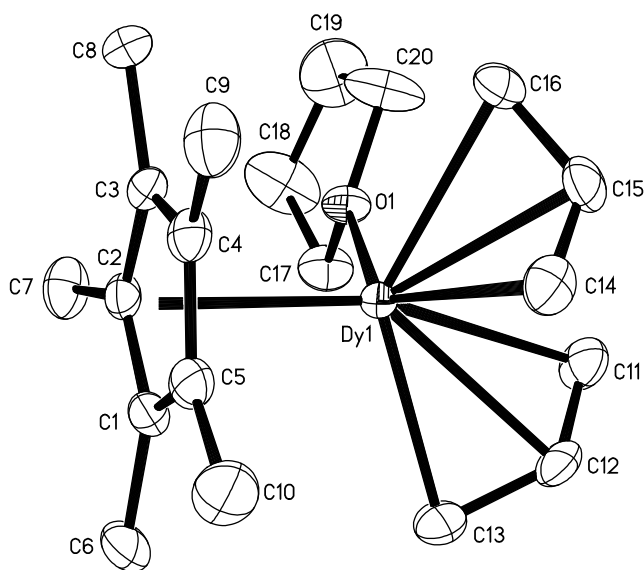


Figure S3. Thermal ellipsoid plot of the bis(allyl) complex $(C_5Me_5)Dy(C_3H_5)_2(THF)$, drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Dy–Cnt (Cnt = C_5Me_5 ring centroid), 2.384; Dy–O, 2.428(2); Dy–C11, 2.749(3); Dy–C12, 2.642(3); Dy–C13, 2.508(3); Dy–C14, 2.686(3); Dy–C15, 2.647(3); Dy–C16, 2.582(3); C11–C12, 1.372(5); C12–C13, 1.401(5); C14–C15, 1.370(5); C15–C16, 1.402(5); Cn1–Dy–O, 102.7; Cnt–Dy–C11, 162.0; Cnt–Dy–C12, 137.9; Cnt–Dy–C13, 108.1; Cnt–Dy–C14, 103.3; Cnt–Dy–C15, 120.5; Cnt–Dy–C16, 109.0.

Reactivity Studies to Identify Original Ammonia Source

We initially explored the possibility that the NH_4Cl used to dehydrate the $DyCl_3(H_2O)_x$ (Scheme S1) was the source of the ammonia ligands found incidentally in **1**. Indeed, since our preparation involves using a 9-fold excess of NH_4Cl to ensure complete conversion to $DyCl_3$, if NH_4Cl was not completely separated by sublimation, it could have been carried along throughout the synthesis to subsequently provide the NH_3 ligands. Whatever its identity, the NH_3 source would need to persist for several synthetic steps to be present in the cation. Elemental analysis of the $DyCl_3$ obtained after the drying process showed no evidence of nitrogen, although IR spectroscopy did show a weak, broad feature near 3300 cm^{-1} .

Crystallographic Details

The structure of the bis(allyl) dysprosium complex $(C_5Me_5)Dy(C_3H_5)_2(THF)$ is compared with that of compositionally similar $(C_5Me_5)Nd(C_3H_5)_2(\text{dioxane})$ ⁴ and with $(C_5Me_5)_2Dy(C_3H_5)^{1,2}$ in Table S1 below. The bond distances in $(C_5Me_5)Dy(C_3H_5)_2(THF)$ are similar to those in $(C_5Me_5)Nd(C_3H_5)_2(\text{dioxane})$, and both complexes exhibit typical Ln–C(allyl) distances that usually involve one short and two longer bond lengths. Interestingly, the Dy–C(allyl) distances in the bis(allyl) species are larger on average and exhibit a greater range than those in $(C_5Me_5)_2Dy(C_3H_5)$, in which each Ln–C(allyl) distance is similar.

Table S1. Comparison of selected bond lengths (Å) of $(C_5Me_5)_2Dy(C_3H_5)^{1,2}$, $(C_5Me_5)Dy(C_3H_5)_2(THF)$, and $(C_5Me_5)Nd(C_3H_5)_2(\text{dioxane})$,⁵ (Cnt = C_5Me_5 ring-centroid).

Complex	Ln–Cnt	Ln–C(allyl)
$(C_5Me_5)_2Dy(C_3H_5)$	2.374 2.359	2.602(3), 2.613(3), 2.596(3)
$(C_5Me_5)Dy(C_3H_5)_2(THF)$	2.384	2.749(3), 2.642(3), 2.508(3) ^a 2.686(3), 2.647(3), 2.582(3) ^b
$(C_5Me_5)Nd(C_3H_5)_2(\text{dioxane})$	2.497	2.79(1), 2.78(1), 2.651(9) 2.75(1), 2.69(1), 2.669(9)

^aFor C(11)–C(13) in that order. ^bFor C(14)–C(16).

Complex $[(C_5Me_5)_2Dy(NH_3)_2][BPh_4]$, **1** has an overall structure like that of many bis(pentamethylcyclopentadienyl) metallocenes.^{1,2,6} Two additional ligands are attached to the metal to give an eight-coordinate complex. The closest ammonia-ligated compounds in the literature for comparison are $(C_5Me_5)_2Yb(SPh)(NH_3)$,^{6k} $(C_5Me_5)_2Yb(TePh)(NH_3)$,⁷ and $(C_5Me_5)_2Yb(THF)(NH_3)$.^{6l} The 2.476(3) and 2.466(3) Å Dy–N distances in the tetraphenylborate complex are comparable to the 2.428(3) and 2.45(1) Å Yb–N distances in $(C_5Me_5)_2Yb(SPh)(NH_3)$ ^{6k} and $(C_5Me_5)_2Yb(TePh)(NH_3)$,⁷ respectively, when the 0.042 Å difference in 8-coordinate ionic radii of Dy^{3+} and Yb^{3+} is considered.⁸ The Dy–N distances in **1** also compare well with the 2.55(3) Å Yb–N distance in $(C_5Me_5)_2Yb(THF)(NH_3)$ ^{6l} considering that 8-coordinate Yb^{2+} has an ionic radius 0.113 Å larger than Dy^{3+} .⁸ The 140.2° (ring centroid)–Ln–(ring centroid) angle in **1** is larger than the 135–137° angles in $(C_5Me_5)_2Yb(SPh)(NH_3)$,^{6k} $(C_5Me_5)_2Yb(TePh)(NH_3)$,⁷ and $(C_5Me_5)_2Yb(THF)(NH_3)$ ^{6l} which probably reflects the small steric demand of two NH_3 ligands compared to the other compounds.

Table S2. Crystallographic details for **1**, **2**, and (C₅Me₅)Dy(C₃H₅)₂(THF).

	1	2	(C ₅ Me ₅)Dy(C ₃ H ₅) ₂ (THF)
Empirical formula	C ₄₄ H ₅₆ BDyN ₂ • ½(C ₇ H ₈)	C ₄₈ H ₆₁ BDyNO	C ₂₀ H ₃₃ DyO
Formula weight	832.28	841.28	451.96
<i>T</i> (K)	100(2)	88(2)	143(2)
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 _{1/n}	<i>P</i> $\bar{1}$
<i>a</i> (Å)	10.144(1)	11.7665(7)	8.564(9)
<i>b</i> (Å)	14.219(2)	22.5380(13)	8.864(9)
<i>c</i> (Å)	28.976(3)	15.3825(9)	13.114(1)
α (°)	81.269(6)	90	84.979(1)
β (°)	84.862(6)	91.7968(7)	76.620(1)
γ (°)	80.791(6)	90	80.143(1)
Volume (Å ³)	4068.5(8)	4077.3(4)	952.91(17)
<i>Z</i>	4	4	2
ρ_{calcd} (Mg/m ³)	1.359	1.370	1.575
μ (mm ⁻¹)	1.871	1.869	3.921
<i>R</i> 1 ^{<i>a</i>}	0.0386	0.0359	0.0231
<i>wR</i> 2 ^{<i>b</i>}	0.0791	0.0620	0.0587

$$^a R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|. \quad ^b wR2 = [\Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]]^{1/2}$$

X-ray Data Collection, Structure Solution and Refinement

For $(\text{C}_5\text{Me}_5)\text{Dy}(\text{C}_3\text{H}_5)_2(\text{THF})$: A yellow crystal of approximate dimensions 0.223 x 0.200 x 0.115 mm was mounted on a glass fiber and transferred to a Bruker SMART APEX II diffractometer. The APEX2⁹ program package was used to determine the unit-cell parameters and for data collection (15 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT¹⁰ and SADABS¹¹ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL¹¹ program. There were no systematic absences nor any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group $P\bar{1}$ was assigned and later determined to be correct. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors¹² for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. At convergence, $wR2 = 0.0601$ and $\text{Goof} = 1.083$ for 204 variables refined against 4354 data (0.74 Å), $R1 = 0.0231$ for those 4119 data with $I > 2.0\sigma(I)$.

For $[(\text{C}_5\text{Me}_5)_2\text{Dy}(\text{NH}_3)_2][\text{BPh}_4]$, **1**: A colorless crystal of approximate dimensions 0.053 x 0.157 x 0.426 mm was mounted on a glass fiber and transferred to a Bruker SMART APEX II diffractometer. As cited above, the APEX2 program package was used to determine the unit-cell parameters and for data collection (10 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT and SADABS to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL program. There were no systematic absences or any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group $P\bar{1}$ was assigned and later determined to be correct. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. Carbon atoms C(17), C(31)-C(40), C(54) and C(55) were disordered and included using multiple components with partial site-occupancy-factors. At convergence, $wR2 = 0.0791$ and $\text{Goof} = 1.073$ for 941 variables refined against 20304 data (0.75 Å), $R1 = 0.0386$ for those 16659 data with $I > 2.0\sigma(I)$.

For $[(\text{C}_5\text{Me}_5)_2\text{Dy}(\text{THF})(\text{NH}_3)][\text{BPh}_4]$, **2**: A colorless crystal of approximate dimensions 0.181 x 0.200 x 0.361 mm was mounted in a cryoloop and transferred to a Bruker

SMART APEX II diffractometer. The APEX2 program package was used to determine the unit-cell parameters and for data collection (20 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT and SADABS to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL program. The diffraction symmetry was $2/m$ and the systematic absences were consistent with the monoclinic space group $P2_1/n$ that was later determined to be correct. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors for neutral atoms were used throughout the analysis. Hydrogen atoms H(1), H(2) and H(3) were located from a difference-Fourier map and refined (x, y, z and U_{iso}). The remaining hydrogen atoms were included using a riding model. At convergence, $wR2 = 0.0620$ and $Goof = 1.028$ for 491 variables refined against 10261 data ($0.74\text{\AA}$), $R1 = 0.0258$ for those 8570 data with $I > 2.0\sigma(I)$.

Definitions:

$$wR2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)]]^{1/2}$$

$$R1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$$

$Goof = S = [\Sigma[w(F_o^2 - F_c^2)^2] / (n-p)]^{1/2}$ where n is the number of reflections and p is the total number of parameters refined.

Additional Magnetic Characterization Data

Arrhenius Plot Fitting Details. The Arrhenius plots for **1** featured a curvature suggesting the presence of multiple relaxation processes. Hence, multiple fits were attempted with different incorporated relaxation pathways, dependent on the sample measurement conditions. The magnetic relaxation pathways commonly considered in the literature, in conjunction with their temperature dependence, are: a temperature-independent quantum tunneling, Direct relaxation ($\propto T$),¹³ Raman relaxation ($\propto T^n$, $n = 4, 5, 7$, or 9 typically),¹⁴ and Orbach relaxation ($\propto \exp(U_{\text{eff}}/k_B T)$). The Arrhenius data for **1** was modeled using Equation S1, and the resulting best-fit parameters are given in Table S3.

$$\frac{1}{\tau_{\text{obs}}} = \frac{1}{\tau_{\text{QTM}}} + AH^2T + CT^n + \tau_0^{-1} \exp\left(-U_{\text{eff}}/k_B T\right) \quad (\text{S1})$$

Here, the first term accounts for quantum tunneling, the second for the Direct process, the third for the Raman process, and the fourth for Orbach relaxation. The Direct term was omitted during fitting of the zero field data, due to its dependence on H , while the quantum tunneling term was omitted when fitting the data collected under 1400 Oe. The best fit to the applied field data was also obtained by excluding the Direct relaxation term. The overall best fit parameters are given below for both zero and applied fields in Table S3. The fit significantly improved by allowing the Raman exponent to vary from the common values of 4, 5, 7, and 9 where this deviation potentially suggests the presence of multiple operating Raman processes, similar to the previously reported fitting procedure employed for $[(\text{C}_5\text{Me}_5)_2\text{Dy}][(\mu\text{-Ph})_2\text{BPh}_2]$.^{6h}

Table S3. Best-fit parameters for the Arrhenius plots of **1**.

H_{dc} (Oe)	τ_{QTM} (s)	C ($\text{s}^{-1}\text{K}^{-n}$)	n	τ_0 (s)	U_{eff} (cm^{-1})
1400 Oe	-	0.00021(3)	4.08(5)	$4(5) \times 10^{-13}$	609(44)
0 Oe	0.00282(2)	0.022(2)	2.86(2)	$2.6(5) \times 10^{-12}$	546(6)

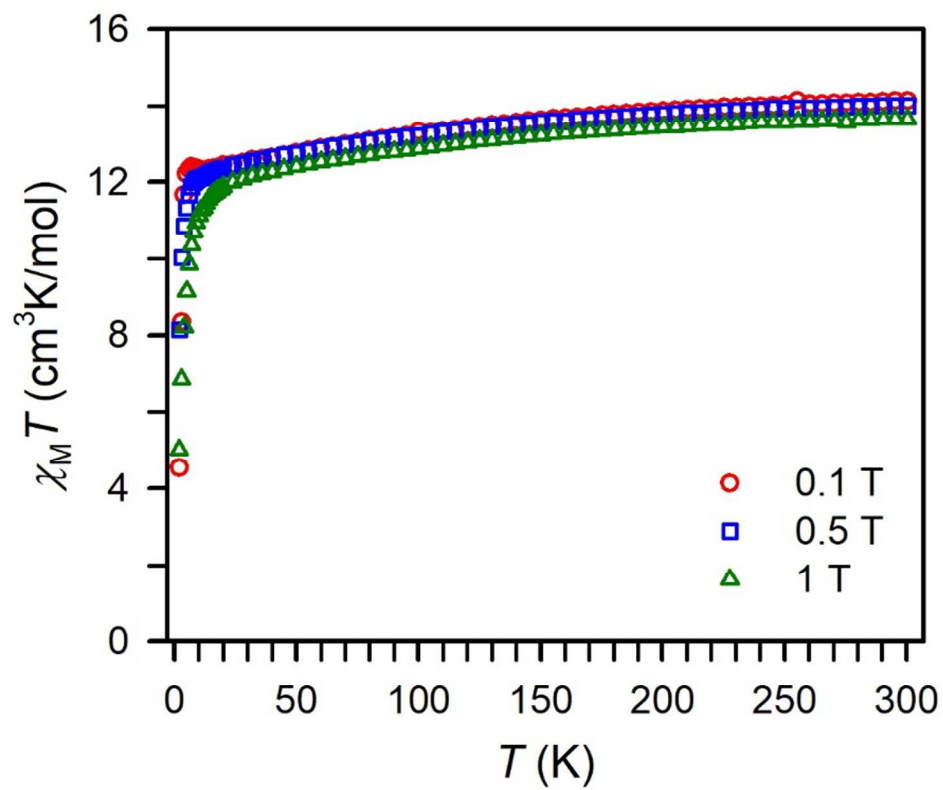


Figure S4. Variable-temperature dc magnetic susceptibility data for a restrained polycrystalline sample of **1** collected under a 1000 Oe (red circles), 5000 Oe (blue squares), and 1 T (green triangles) applied dc field.

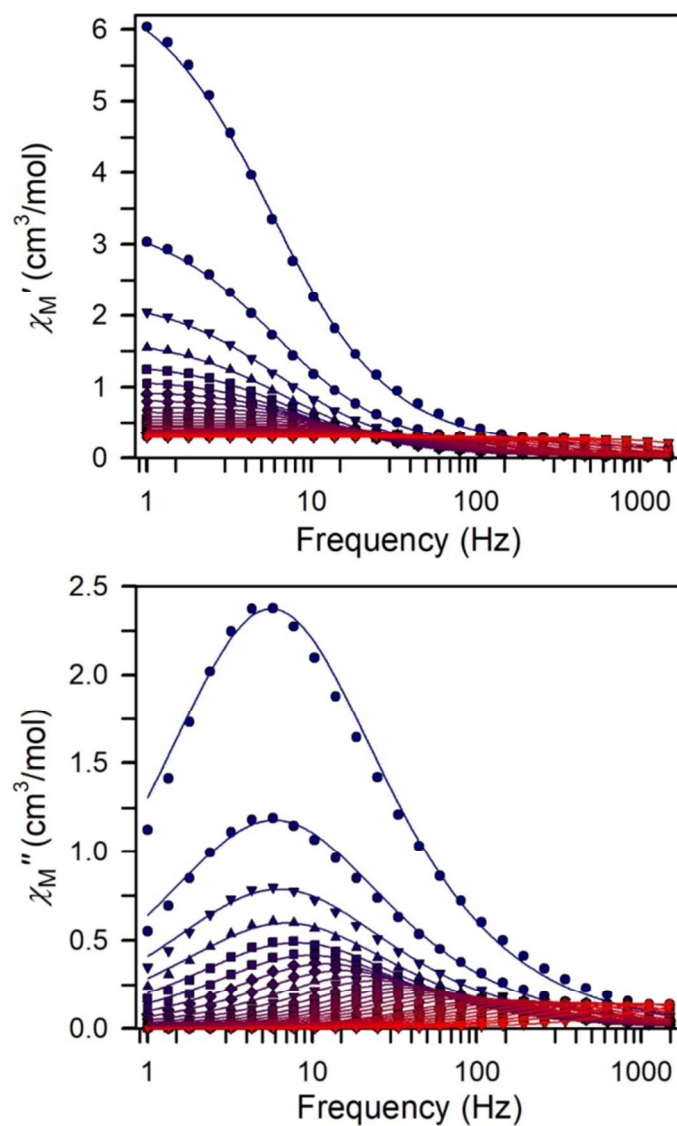


Figure S5. In-phase (χ_M' , top) and out-of-phase (χ_M'' , bottom) components of the ac magnetic susceptibility for **1** under zero dc field from 2 K (blue circles) to 46 K (red circles). Solid lines represent fits to the data, as described in the main text.

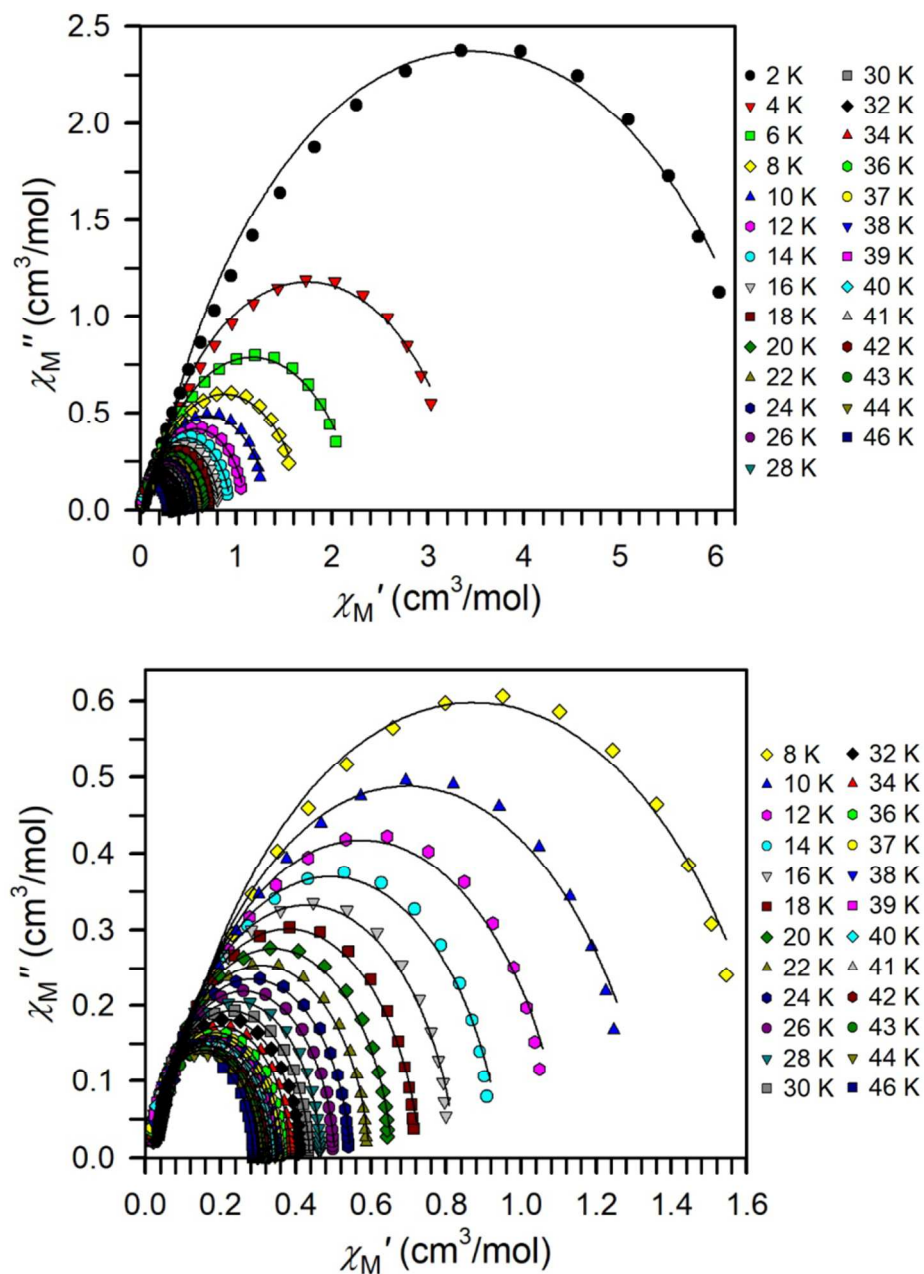


Figure S6. Cole-Cole (Argand) plots for ac susceptibility collected under zero applied dc field for **1** from 2 to 46 K (top) and expanded in the high-frequency region to better show 8-46 K data (bottom). Symbols represent the experimental data points and the points representing the fits are connected by solid black lines.

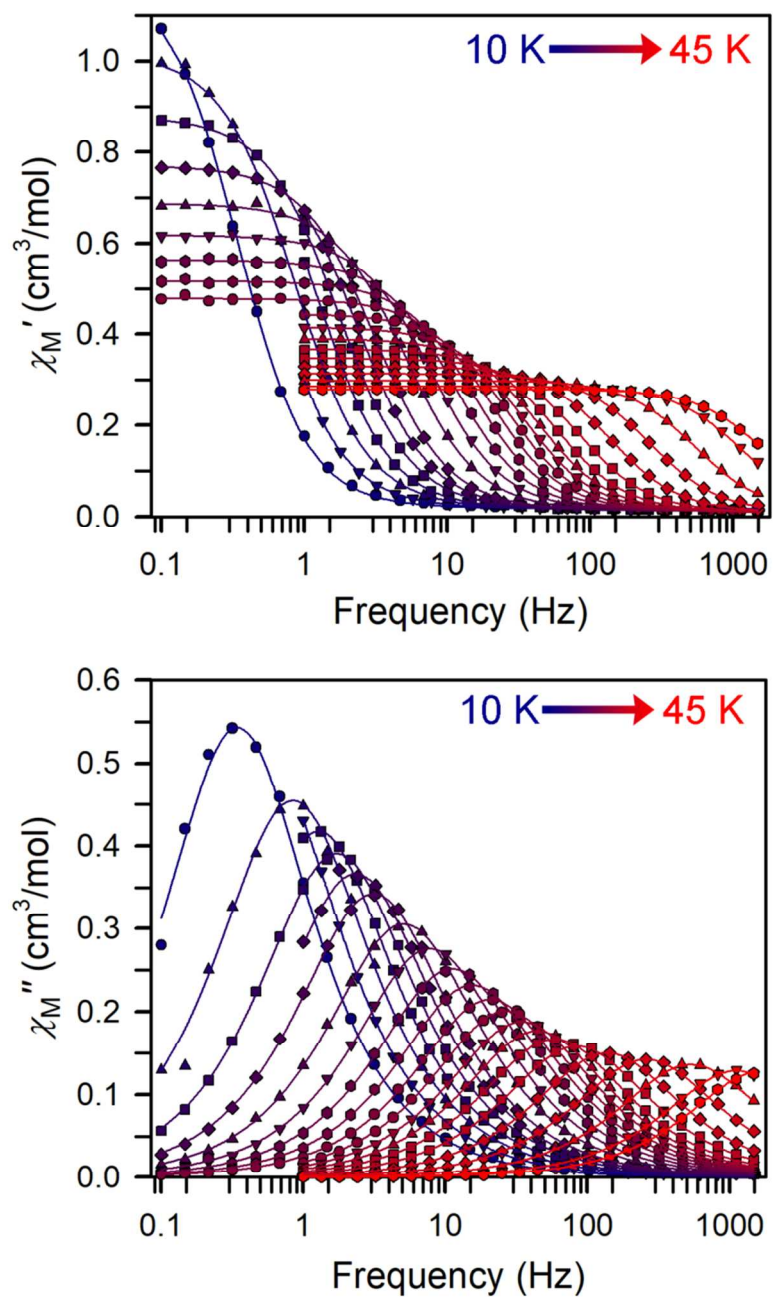


Figure S7. Top: In-phase (χ_M' , top) and out-of-phase (χ_M'' , bottom) components of the ac magnetic susceptibility for **1** measured under a 1400 Oe dc field from 10 K (blue circles) to 45 K (red circles). Solid lines represent fits to the data as described in the main text.

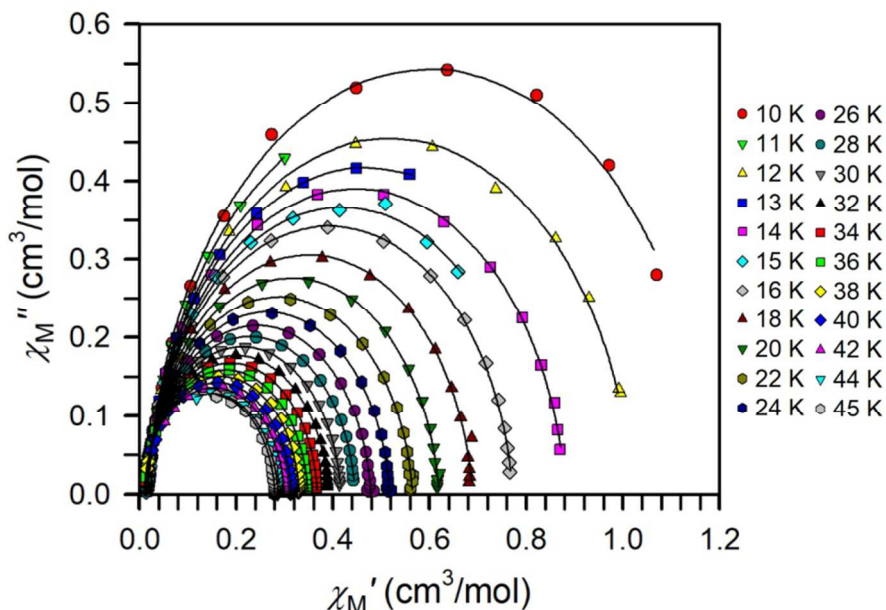


Figure S8. Cole-Cole (Argand) plots for ac susceptibility collected under a 1400 Oe dc field for **1** from 10 to 45 K. Symbols represent the experimental data points and the points representing the fits are connected by solid black lines.

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