A Comparison of the Effects of Symmetry and Magnetoanisotropy on Paramagnetic Relaxation in Related Dysprosium Single Ion Magnets

Ursula J. Williams, Brian D. Mahoney, Patrick T. DeGregorio, Patrick J. Carroll, Eiko Nakamaru-Ogiso, James M. Kikkawa, and Eric J. Schelter

P. Roy and Diana T. Vagelos Laboratories, Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104

E-mail: schelter@sas.upenn.edu

Electronic Supplementary Information

Experimental Procedures

General Methods. Unless otherwise indicated all reactions and manipulations were performed under an inert atmosphere (N_2) using standard Schlenk techniques or in a Vacuum Atmospheres, Inc. Nexus II drybox equipped with a molecular sieves 13X / Q5 Cu–0226S catalyst purifier system. Glassware was oven-dried overnight at 150 °C prior to use. ^{1}H–NMR spectra were obtained on a Bruker DMX–300 Fourier transform NMR spectrometer at 300 MHz. EPR spectra were recorded by a Bruker Elexsys 500 spectrometer at X-band (9.4 GHz), a microwave power of 1 mW, a modulation frequency of 100 kHz, and a modulation amplitude of 20 G. The temperature of the EPR experiments was held at 5 K using an Oxford Instrument ESR900 helium flow cryostat. EPR analyses were performed on solids after grinding them to fine powders. Solution phase EPR measurements were attempted in THF/toluene glasses, but were precluded due to the poor solubility of **4** and **6** during the preparation of the glasses. ^{1}H-NMR chemical shifts were recorded in units of parts per million downfield from residual proteo solvent. Elemental analyses were performed at the University of California, Berkeley Microanalytical Facility using a Perkin-Elmer Series II 2400 CHNS analyzer.

Materials. Tetrahydrofuran, dimethoxyethane, and toluene were purchased from Fisher Scientific. The solvents were sparged for 20 min with dry N_2 and dried using a commercial two-column solvent purification system comprising two columns of neutral alumina. Methanol was purchased from Fisher Scientific and used as received. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc. and dried over potassium mirror for 16 h prior to use. Nickel(II) acetate tetrahydrate, *o*–phenylenediamine, and 2,4–pentanedione were purchased from Acros Organics and used as received. HCl gas was purchased from Airgas, Inc. and used as received. Triethylamine was purchased from Fisher Scientific and used as received. Anhydrous dysprosium(III) chloride and yttrium(III) chloride were purchased from Strem Chemicals, Inc.

and used as received. 18-crown-6 was purchased from Acros Organics, recrystallized from acetonitrile, and dried under reduced pressure at room temperature for 24 hours.

X-Ray Crystallography. X-ray intensity data were collected on a Bruker APEXII CCD area detector employing graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) at a temperature of 143(1) K. In all cases, rotation frames were integrated using SAINT,[1] producing a listing of unaveraged F^2 and $\sigma(F^2)$ values which were then passed to the SHELXTL[2] program package for further processing and structure solution on a Dell Pentium 4 computer. The intensity data were corrected for Lorentz and polarization effects and for absorption using TWINABS[3] or SADABS.[4] The structures were solved by direct methods (SHELXS-97).[5] There were several areas of disordered solvent for which reliable disorder models could not be devised; the X-ray data were corrected for the presence of disordered solvent using SQUEEZE.[5] Refinement was by full-matrix least squares based on F^2 using SHELXL-97.[5] All reflections were used during refinements. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a riding model.

Static Magnetic Susceptibility Measurements. Static magnetic data were collected using a Quantum Design Multi-Property Measurement System (MPMS–7) with a Reciprocating Sample Option at 0.1 T from 2–300 K and at 2 K from 0–7 T. Gelatin capsules were used to hold the samples for measurement. Eicosane was added to the gelatin capsule and massed to the nearest 0.1 mg in an inert atmosphere (N_2) drybox using a calibrated and leveled Mettler-Toledo AL-204 analytical balance. Next, the sample was added to the capsule and massed to the nearest 0.1 mg. The capsule was supported in a copper wire cable and heated until the wax melted, creating a suspension of the sample. Upon cooling to room temperature, the suspended samples became fixed in the wax. The sample and wax, contained in the closed gelatin capsules and

enclosed in drinking straws for measurement, were transferred to the MPMS under inert atmosphere and immediately loaded into the inert atmosphere of the measurement chamber with three evacuation/purge cycles. Corrections for the intrinsic diamagnetism of the samples were made using Pascal's constants.[6] The measurements of **3** and **4** were made in duplicate on independently prepared samples.

Dynamic Magnetic Susceptibility Measurements. Dynamic magnetic data were collected using a Quantum Design Physical Property Measurement System (PPMS) equipped with a 9 Tesla magnet and an AC/DC Magnetometry System (ACMS) from 2–15 K at 0 T and 0.1 T applied DC fields and 3 Oe AC field amplitude for frequencies of 250, 628, 1581, 3976, and 10,000 Hz. The magnetic fields of 0 T and 0.1 T were set using linear mode; residual fields of ± 20 Oe may have been present due to trapped flux.[7] The samples, chemically identical to those used in the EPR experiments, were prepared and loaded in an identical fashion to those prepared for the static measurements.

Synthetic Details and Characterization

Synthesis of H_2tmtaa. Tetramethyldibenzotetraaza[14]annulene (**(**H_2tmtaa) was synthesized with modifications to the previously reported procedures in order to eliminate trace amounts of Ni(tmtaa) from the isolated H_2tmtaa.[8, 9] Ni(tmtaa) was synthesized as previously described.[8] 9.41 g Ni(tmtaa) was suspended in 100 mL CH_3OH, and HCl gas was bubbled through the mixture at atmospheric pressure for ~5 minutes, producing a white precipitate and a dark brown supernatant. The reaction mix was chilled at –35^o C and the white product collected by filtration over a Büchner funnel. The white solid was washed 3 × 25 mL cold CH_3OH and dried under reduced pressure, yielding the hydrochloride salt: H_2tmtaa•2HCl. Yield 8.72 g, 20.89

mmol, 89 %. In order to eliminate any trace amounts of H_4tmtaa•[$NiCl_4$] prior to treatment of H_2tmtaa•2HCl with NEt_3, a metathesis reaction was performed using NH_4PF_6. The white H_2tmtaa•2HCl isolated during the acidification step (6.75 g, 16.18 mmol) was dissolved in 100 mL H_2O and an aqueous solution of NH_4PF_6 (5.77 g, 35.37 mmol, 2.2 equiv) dissolved in 50 mL H_2O was slowly added with stirring, inducing the precipitation of a white solid (H_4tmtaa•2PF_6). The solid H_4tmtaa•2PF_6 was isolated by filtration over a Büchner funnel, washed with 100 mL H_2O, and dried under reduced pressure. A CH_3OH slurry of the white solid was prepared and NEt_3 was added until the solution reached a pH of 9 and a yellow precipitate was observed. The powder was isolated over a Büchner funnel, washed 3 × 10 mL CH_3OH, and dried under dynamic vacuum. Yield: 3.74, 10.87 mmol, 67 %. The NMR resonances observed for H_2tmtaa were consistent with reported values.[10] We noted in several other attempted syntheses of H_2tmtaa that direct treatment of H_2tmtaa•2HCl with NEt_3 yielded a yellow-green product from the presence of trace amounts of Ni(tmtaa), which is produced when H_4tmtaa•[$NiCl_4$] reacts with NEt_3.

Synthesis of K_2tmtaa. In a procedure adapted from Magull *et al*,[11] KH (1.05 g, 26.13 mmol) was added to a stirred, clear yellow solution of H_2tmtaa (2.97 g, 8.63 mmol, 0.33 equiv) in 50 mL THF. The solution became dark red with stirring. The reaction mixture was stirred for 16 h. The dark red reaction mixture was filtered through a Celite-packed, coarse porosity fritted filter and the solvent removed under reduced pressure to produce a red solid. The solid was collected, washed with hexanes and dried under reduced pressure. Yield: 3.50 g, 8.32 mmol, 95 %. ^{1}H NMR (300 MHz, THF-d_8) δ: 6.52 (m, 8H, Ar–*H*), 4.20 (s, 2H, –C*H*), 1.96 (s, 12H, –CH_3).

Synthesis of [K(DME)$_2$][Y(tmtaa)$_2$] (2). Anhydrous YCl_3 (0.47 g, 2.38 mmol) was added to a stirred solution of K_2tmtaa (2.00 g, 4.76 mmol, 2.0 equiv) in 40 mL DME. The

resulting solution changed from red to orange on stirring for 16 h at room temperature. The reaction mixture was concentrated to ~20 mL under reduced pressure and heated to dissolve solids. After standing undisturbed at room temperature for ~1 hr, the reaction mixture was filtered to remove KCl precipitate. The filtrate solution was chilled overnight at –35 ^{o}C and the resultant orange crystalline solid was isolated and washed 2 × 5 mL DME. In order to maintain both equivalents of coordinated solvent, the crystals were atmosphere-dried under N_2 rather than exposed to reduced pressure. Yield: 0.77 g, 0.80 mmol, 34 %. Rigorous drying of the crystals under reduced pressure desolvated one equivalent of DME, yielding the complex of formula: [K(DME)][Y(tmtaa)$_2$]. Anal. Calcd. for $KYC_{48}H_{54}N_8O_2$: C, 63.84; H, 6.03; N, 12.41. Found: C, 63.55; H, 6.16; N, 12.28. ^{1}H NMR (300 MHz, THF-d_8): δ 6.97 (m, 8H, Ar–*H*), 6.85 (m, 8H, Ar–*H*), 3.98 (s, 4H, –C*H*), 3.49 (s, 4H, OCH_2), 3.33 (s, 6H, OCH_3), 1.88 (s, 24H, –CH_3).

Synthesis of [K(DME)$_2$][Dy(tmtaa)$_2$] (3). Anhydrous $DyCl_3$ (0.068 g, 0.25 mmol) was added to a stirred solution of K_2tmtaa (0.21 g, 0.49 mmol, 2.0 equiv) in 10 mL DME. The resulting solution changed from red to orange on stirring 16 h at room temperature. The reaction mixture was concentrated under reduced pressure and warmed to dissolve suspended solids and saturate the solution. After standing undisturbed at room temperature for ~1 hr, the reaction mixture was filtered to remove KCl precipitate. The filtrate solution was chilled overnight at –35 ^{o}C and the resultant orange crystalline solid was isolated, washed 2 × 5 mL DME. In order to maintain both equivalents of coordinated solvent, the crystals were atmosphere-dried under N_2 rather than exposed to reduced pressure. Yield: 0.10 g, 0.095 mmol, 37 %. Anal. Calcd. for $KDyC_{52}H_{64}N_8O_4$: C, 58.55; H, 6.05; N, 10.51. Found: C, 58.79; H, 6.03; N, 10.95. ^{1}H NMR (300 MHz, THF-d_8) δ: 68.23 (broad s), 9.89 (broad s), –69.06 (broad s), –89.82 (broad s). Definitive

^{1}H-NMR peak assignments could not be made due to fast paramagnetic relaxation and broadening of the proton resonances.

Synthesis of [K(DME)(18-crown-6)][Dy(tmtaa)$_2$] (4). A solution of 18-crown-6 (0.008 g, 0.030 mmol) in 1 mL toluene was added slowly to a solution of [K(DME)$_2$][Dy(tmtaa)$_2$] (0.027 g, 0.025 mmol, 0.83 equiv) in 7 mL DME. Upon standing at room temperature, orange crystals grew from the solution mixture. The mother liquor was decanted off and the crystals were washed 3 × 3 mL DME, then dried under reduced pressure. Yield: 0.020 g, 0.016 mmol, 64 %. Anal. Calcd. for $KDyC_{60}H_{78}N_8O_4$: C, 58.07; H, 6.34; N, 9.03. Found: C, 57.76; H, 6.12; N, 8.83. ^{1}H NMR (THF-d$_8$): δ 59.36 (broad s), 52.60 (broad overlapping s, 16H total, Ar–*H*), 14.09 (broad s, 24H, C*H*$_3$), –84.54 (broad s, 4H, C*H*). The –C*H*$_2$ resonance of the 18–crown-6 was observed to overlap with a proteo-THF peak at 1.73 ppm.

Preparation of [K(DME)$_2$][Y(tmtaa)$_2$]$_{0.95}$[Dy(tmtaa)$_2$]$_{0.05}$ (5). [K(DME)$_2$][Y(tmtaa)$_2$] (0.19 g, 0.19 mmol) and [K(DME)$_2$][Dy(tmtaa)$_2$] (0.010 g, 0.009 mmol, 0.05 equiv) were suspended in 20 mL DME and the solution was heated gently to dissolve the solids. The solution was then set undisturbed to cool to room temperature, followed by chilling at –35 ^{o}C for 16 h. The mother liquor was decanted away from the resultant orange crystalline solid, which was then washed 2 × 5 mL DME. In order to maintain both equivalents of coordinated solvent, the crystals were atmosphere-dried under N_2 rather than exposed to reduced pressure. Yield: 0.14 g, 0.14 mmol, 73 %. The dopant level of **5** was verified empirically to be ~6% by comparison of the χ_m' signal at 2 K, 250 Hz, 0 Oe (Figure S4) to the χ_m' signal of **3** under the same experimental conditions (Figure S2).[12]

Preparation of [K(DME)(18-crown-6)][Y(tmtaa)$_2$]$_{0.95}$[Dy(tmtaa)$_2$]$_{0.05}$ (6). A solution of 18-crown-6 (0.018 g, 0.068 mmol) in 2 mL toluene was added slowly to a solution of

$[K(DME)_2][Y(tmtaa)_2]_{0.95}[Dy(tmtaa)_2]_{0.05}$ (0.061 g, 0.061 mmol) in 15 mL DME. Upon standing at room temperature, orange crystals precipitated from the reaction mixture. The crystals were isolated by vacuum filtration over a medium porosity fritted filter, washed 3 × 3 mL DME, and dried under reduced pressure. Yield: 0.040 g, 0.034 mmol, 56 %. The dopant level of **6** was verified empirically to be ~4% by comparison of the χ_m' signal at 2 K, 250 Hz, 0 Oe (Figure S4) to the χ_m' signal of **4** under the same experimental conditions (Figure S3).[12]

Dy(1)N(1)	**Dy(1)-N(2)**	**Dy(1)-N(3)**	**Dy(1)-N(4)**	**Dy(1)-N(5)**	**Dy(1)-N(6)**	**Dy(1)-N(7)**	**Dy(1)-N(8)**
2.507(5)	2.484(4)	2.482(5)	2.461(5)	2.444(5)	2.425(5)	2.442(5)	2.449(4)
K(1)-N(1)	**K-N(2)**	**K(1)-N(3)**	**K(1)-N(4)**				
2.981(5)	2.973(5)	3.069(5)	3.084(5)				

Table S1. Important crystallographic bond lengths in compound **3**.

Dy(1)-N(1)	**Dy(1)-N(2)**	**Dy(1)-N(3)**	**Dy(1)-N(4)**
2.4503(11)	2.4534(12)	2.4581(12)	2.4423(12)

Table S2. Important crystallographic bond lengths in compound **4**.

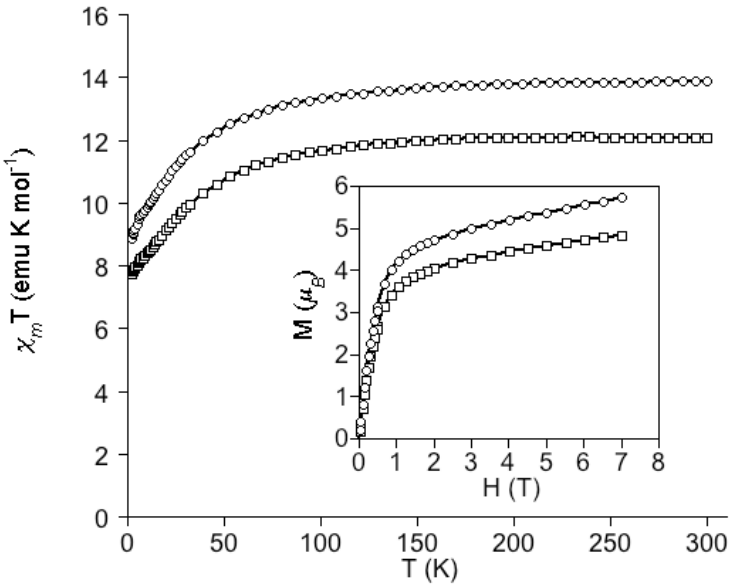

Figure S1. Temperature dependent static magnetic susceptibility characterization of **3** (○) and **4** (□) from 2-300 K in the presence of a 0.1 T applied field. Compound **3** attains a room temperature magnetic moment of 13.89 emu K mol^{-1}, consistent with the predicted Curie value of 14.18 emu K mol^{-1} for the dysprosium(III) ion with a $^{6}H_{15/2}$ ground state.[13] Temperature dependent measurement of **4** reveals a room temperature χT value of 12.08 emu K mol^{-1}, somewhat lower than the expected value, but consistent over multiple experiments. The decrease in the χT products with decreasing temperature for **3** and **4** are due to depopulation of crystal field sublevels. Inset shows field dependent susceptibility data for both compounds from 0–7 T at 2 K. The field dependent data of compound **4** shows a similarly lower moment than compound **3** at all fields greater than 0 T. Lines are a guide for the eye.

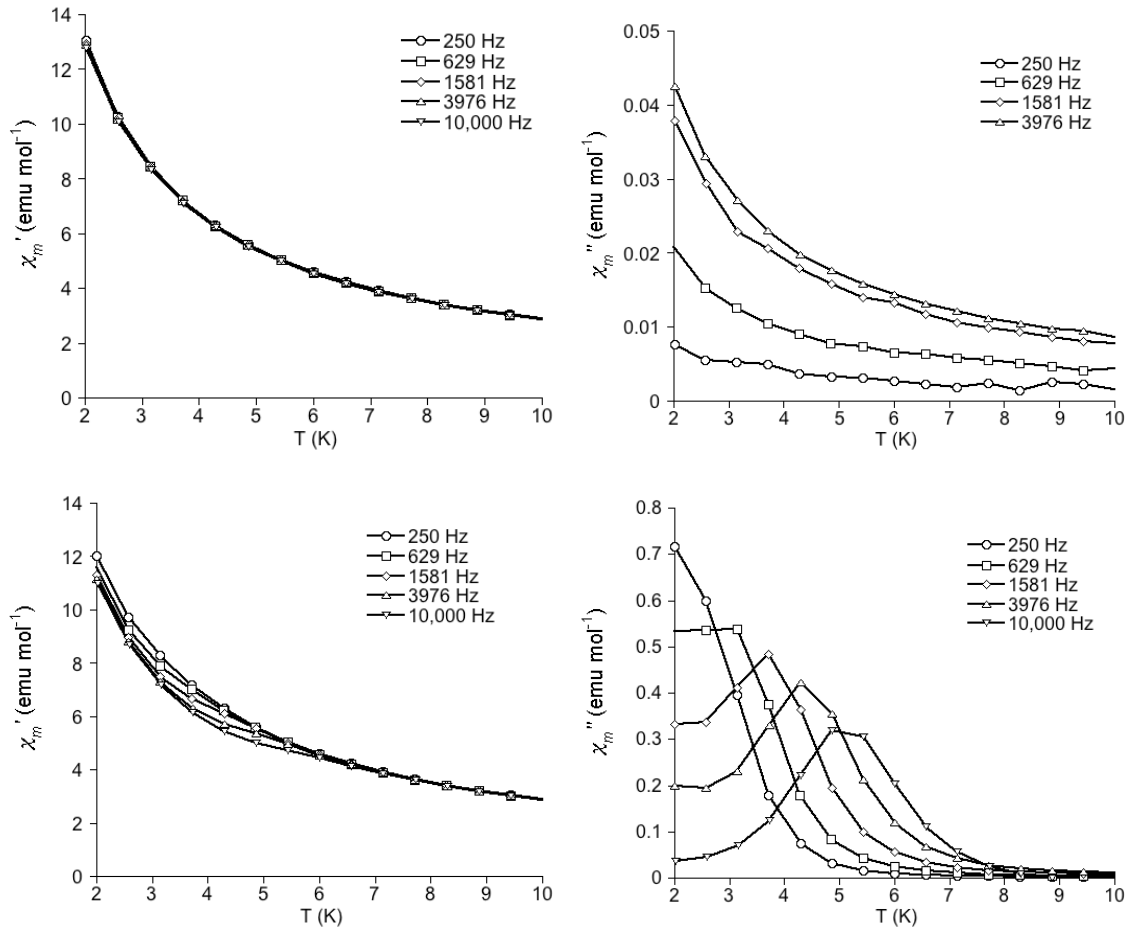

Figure S2. In-phase (left) and out-of-phase (right) magnetic susceptibility data for **3** collected at applied fields of 0 Oe (top) and 100 Oe (bottom). Lines are a guide for the eye.

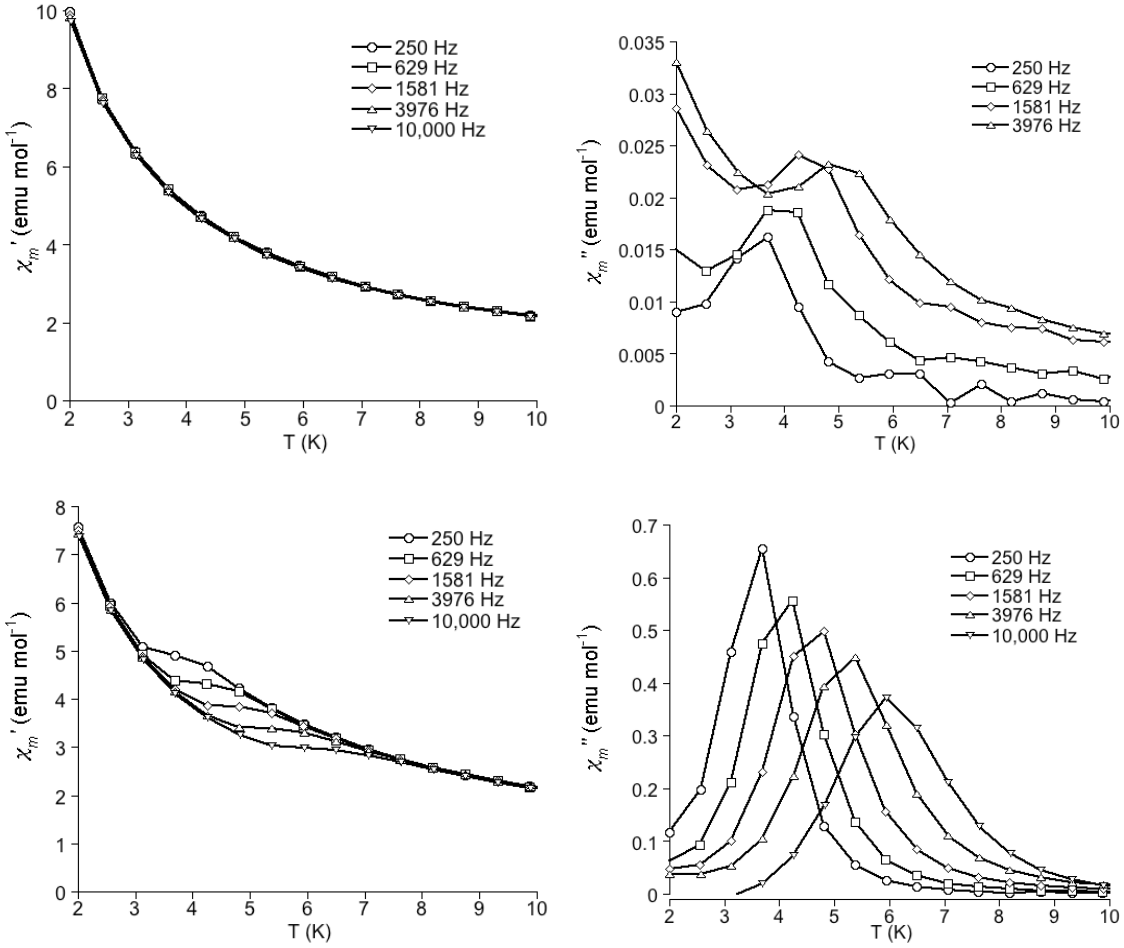

Figure S3. In-phase (left) and out-of-phase (right) magnetic susceptibility data for **4** collected at applied fields of 0 Oe (top) and 100 Oe (bottom). Lines are a guide for the eye.

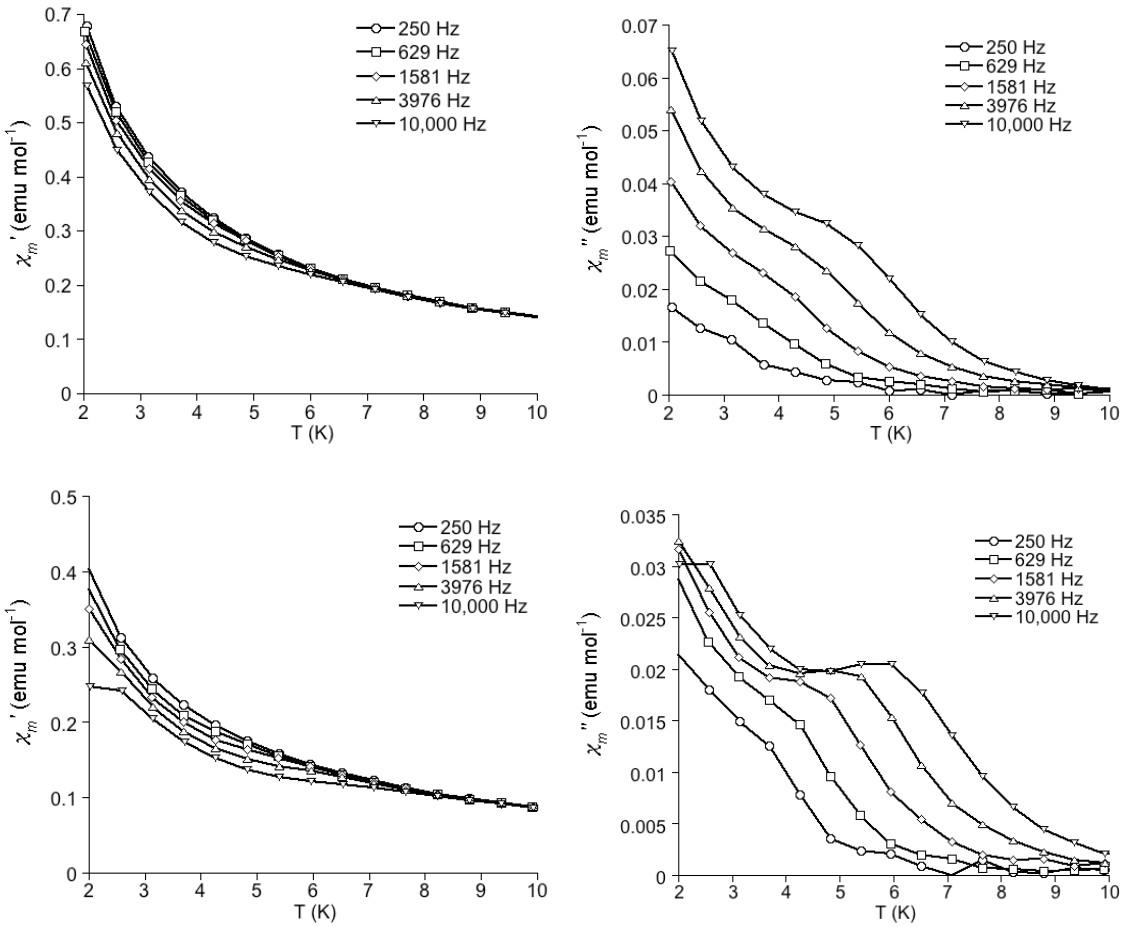

Figure S4. In-phase (left) and out-of-phase (right) magnetic susceptibility data for **5** (top) and **6** (bottom) collected at 0 Oe applied field. Lines are a guide for the eye.

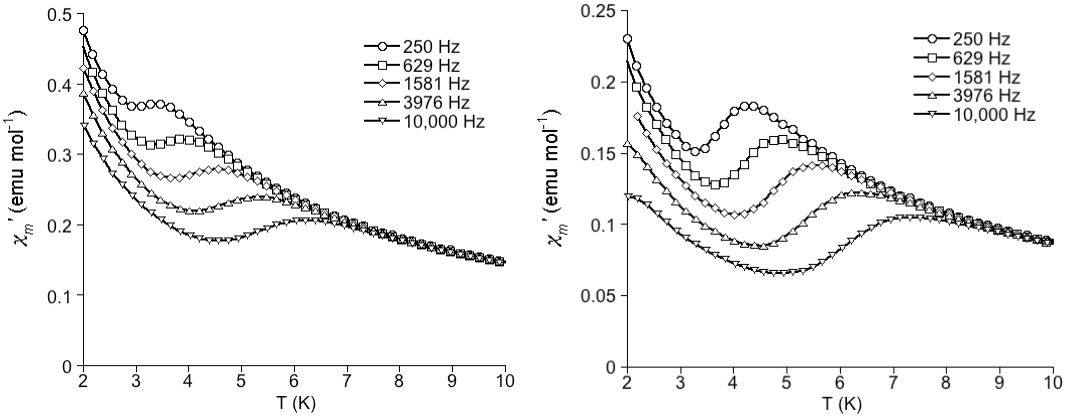

Figure S5. In-phase magnetic susceptibility data for **5** (left) and **6** (right) collected at 100 Oe applied field. Lines are a guide for the eye.

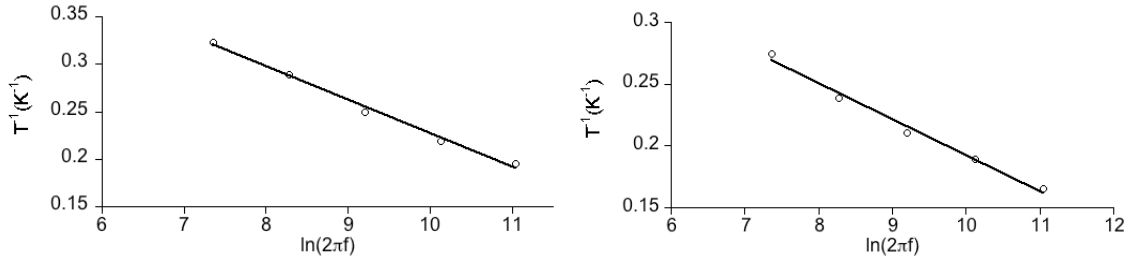

Figure S6. Arrhenius plots constructed from the out-of-phase magnetic susceptibility data for **5** (left) and **6** (right). Lines represent linear fits to the data.

References

1. Bruker, SAINT, Bruker AXS, Inc., Madison, WI, USA, 2009.
2. Bruker, SHELXTL, Bruker AXS, Inc., Madison, WI, USA, 2009.
3. G. M. Sheldrick, TWINABS, University of Gottingen, Germany, 2008.
4. G. M. Sheldrick, SADABS, University of Gottingen, Germany, 2007.
5. G. Sheldrick, *Acta Crystallog. Sect. A*, 2008, **64**, 112-122.
6. G. A. Bain and J. F. Berry, *J. Chem. Educ.*, 2008, **85**, 532.
7. Quantum Design, *Using PPMS Superconducting Magnets at Low Fields*. Application Note 1070-207, http://www.qdusa.com/sitedocs/appNotes/ppms/1070-207.pdf. 2009.
8. V. L. Goedken, M. C. Weiss, D. Place and J. Dabrowiak, *Inorg. Synth.*, 2007, 115-119.
9. J. H. Niewahner, K. A. Walters and A. Wagner, *J. Chem. Educ.*, 2006, **84**, 477-479.
10. K. Sakata, J. Yamashita, M. Hashimoto, A. Tsuge and Y. Tanoue, *J. Heterocycl. Chem.* 2001, **38**, 933-938.
11. J. Magull and A. Simon, *Z. Anorg. Allg. Chem.* 1992, **615**, 81-85.
12. K. R. Meihaus, J. D. Rinehart and J. R. Long, *Inorg.Chem.*, 2011, **50**, 8484-8489.
13. C. Benelli and D. Gatteschi, *Chem. Rev.* 2002, **102**, 2369-2387.