Electronic Supplementary Information (ESI)

Structural and Magnetic Conformation of a Cerocene $[Ce(COT")_2]^-$ Exhibiting a Uniconfigurational f^1 Ground State and Slow-Magnetic Relaxation

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1. Experimental procedures

1.1. General considerations

Unless specified otherwise, all manipulations were performed under an inert atmosphere using standard Schlenk or glove box techniques. Glassware was oven dried (120 ºC, 6 h) before use. Hexanes, and dimethoxyethane (DME) were dried using activated alumina and stored over 3 Å molecular sieves. All chemicals were purchased from Thermofisher Scientific or Strem and used without further purification. The $[Li_4(COT")_2(THF)_4]$ was synthesized using a previously published procedure.[1] ^1H and ^{13}C spectra were recorded on a 300 MHz Bruker Advance spectrometer at room temperature (21-23 °C). THF-d_8 was dried over sodium metal for 24 h, distilled, then stored over 3 Å molecular sieves. IR data were collected on a Varian 640 FT-IR spectrometer.

1.2. Synthesis of $Li(DME)_3[Ce(COT")_2]$

To a 20 mL scintillation vial $CeCl_3$ (0.045 g, 0.183 mmol) and $[Li_4(COT")_2(THF)_4]$ (0.218 g, 0.274 mmol) were added. The reagents were stirred in 7 mL of DME at room temperature for 36 h. After 36 h, 2 mL of hexanes was added to the solution while stirring and the precipitate (LiCl) was immediately filtered off through a fine fritted funnel containing Celite. Large green block crystals suitable for X-ray diffraction were grown from a concentrated solution (1:1 DME:hexanes) providing $Li(DME)_3[Ce^{III}(COT'')_2]$ in 67% yield. The isolated crystals were

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[1] M. Jeletic, F. Perras, S. Gorelsky, J. Le Roy, I. Korobkov, D. Bryce, M. Murugesu, *Dalton Trans*., **2012**, *41*, 8060.

extremely air and moisture sensitive. Selected IR data for **1** (cm^{-1}): 2950 (br), 2892 (m), 1447 (w), 1244 (s), 1079 (w), 1049 (s), 979 (w), 932 (m), 907 (w), 834 (s), 749 (m), 722 (m), 680 (w), 635 (w).

1.3. Characterisation

X-Ray Crystallography

Single crystals of **1** were grown from a concentrated solution of 1:1 DME:hexanes. Large green block crystals were additionally washed with hexanes. For **1**, a suitable prism shaped crystal was mounted in inert oil and transferred to the cold gas stream of the diffractometer. Unit cell measurements and intensity data were collected at 200 K on a Bruker-AXS SMART 1 k CCD diffractometer using graphite monochromated MoK_{α} radiation (λ = 0.71073 Å). The data reduction included a correction for Lorentz and polarization effects, with an applied multi-scan absorption correction (SADABS).[2] The crystal structure was solved and refined using the SHELXTL[3] program suite. Direct methods yielded all non-hydrogen atoms, which were refined with anisotropic thermal parameters. All hydrogen atom positions were calculated geometrically and were riding on their respective atoms. The crystal structure has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number CCDC 944915.

1.4. Electrochemistry

Voltammetry experiments were performed using a CH Instruments 620D Electrochemical Analyzer/Workstation and the data were processed using CHI software v 9.24. All experiments were performed in an N_2 atmosphere drybox using electrochemical cells that consisted of a 4 mL vial, platinum disc (2 mm diameter) working electrode, a platinum wire counter electrode, and a silver wire plated with AgCl as a quasi-reference electrode. The working electrode surfaces were polished prior to each set of experiments, and were periodically replaced on scanning > 0 V versus ferrocene (Fc) to prevent the build-up of oxidized product on the electrode surfaces. Solutions employed during the CV studies were ~1 mM in analyte and 0.1 M in $[^{n}Pr_4N][B(3,5\text{-}(CF_3)_2\text{-}C_6H_3)_4]$ ($[^{n}Pr_4N][BAr^F_4]$). Potentials were reported *versus* Fc, which was added as an

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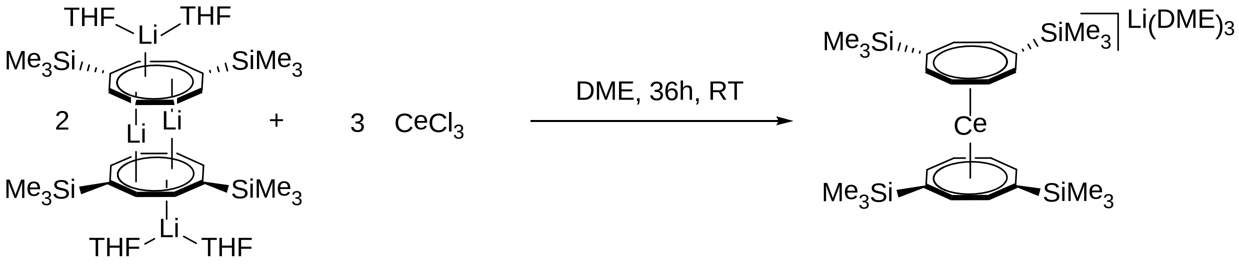
[2] G. M. Sheldrick, SADABS — Bruker AXS area detector scaling and absorption, version 2008/1, University of Göttingen, Germany **2008**.

[3] G. M. Sheldrick, *Acta Cryst.* **2008**, *A64*, 112.

internal standard for calibration at the end of each run. All data were collected in a positive-feedback IR compensation mode. The THF solution cell resistances were measured prior to each run at ~1100 Ω. Scan rate dependences of 50–1000 mV/s were performed to determine electrochemical reversibility. The ΔE_p values recorded were reproducible with variable analyte and electrolyte concentrations. Additionally, the observed ΔE_p for Fc at a scan rate of 100 mV/s was no greater than 80 mV. The Randels–Sevcik equation was plotted using associated scan rate data.

1.5. Magnetism

Magnetic susceptibility measurements for **1** were obtained using a Quantum Design SQUID magnetometer MPMS-XL7 operating between 1.8 and 300 K for DC applied fields ranging from -7 to 7 T. DC analyses were performed on polycrystalline samples sealed in a polyethylene membrane (prepared in an inert atmosphere) under a field ranging from 0 to 7 T and temperatures between 1.8 and 300 K. AC susceptibility measurements were carried out under an oscillating ac field of 3 Oe and ac frequencies ranging from 1 to 1500 Hz and dc fields ranging from 0 to 1600 Oe. Magnetization data was collected at 100 K to check for ferromagnetic impurities that were absent. Diamagnetic corrections were applied for the sample holder and the core diamagnetism from the sample (estimated with Pascal constants).



Scheme S1. Synthetic route to **1**, solid state complex is isolated upon 50% v/v addition of hexanes.

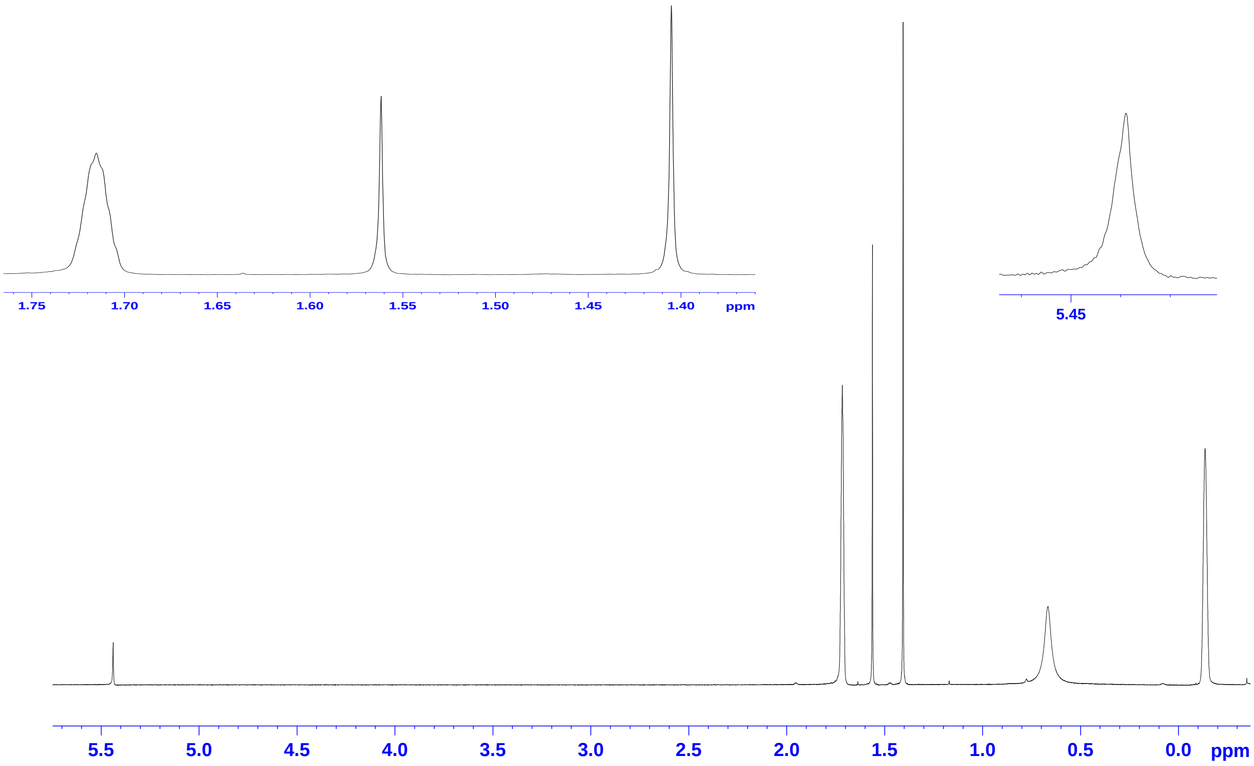


Fig. S1. ^{1}H NMR (300 MHz, THF-d_8) spectrum **1**, the insets show the expanded (horizontal scale) signals.

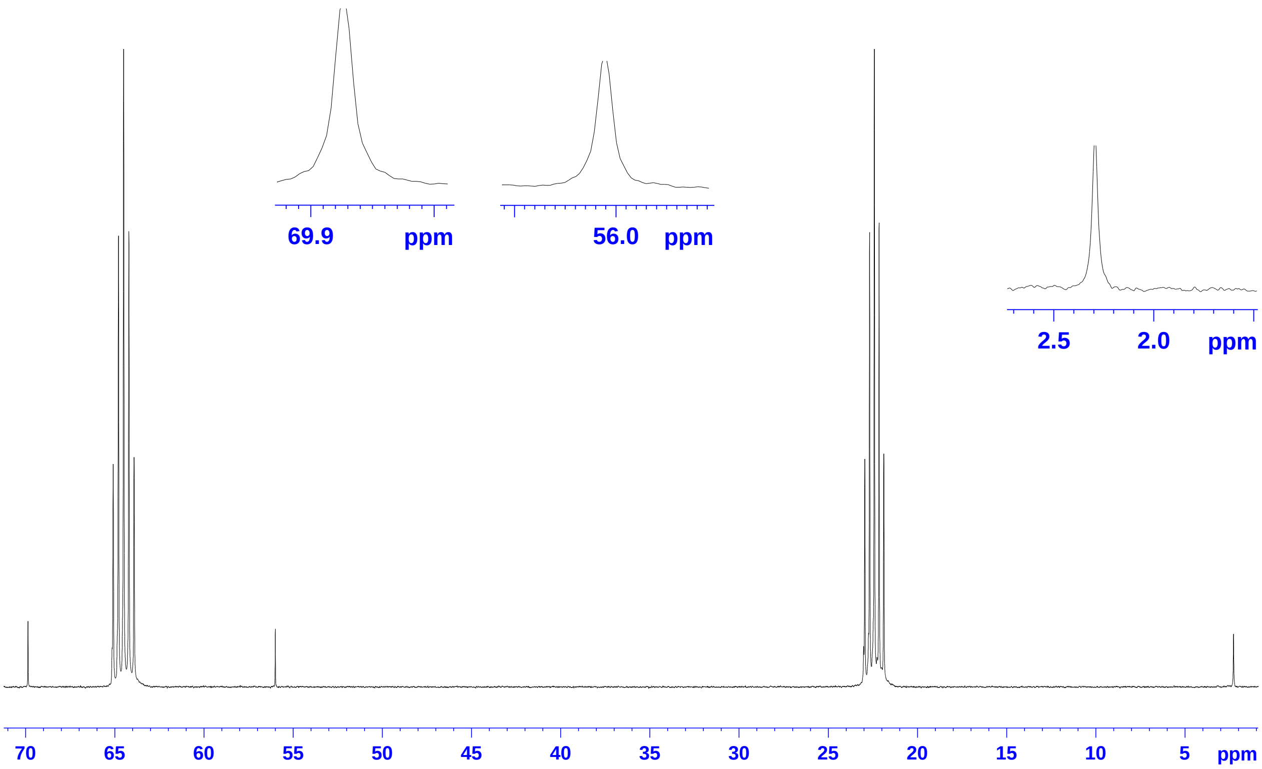


Fig. S2. ^{13}C NMR (300 MHz, δ 64.55(q), 22.43(q), THF-d_8) spectrum **1**, the insets show the expanded (horizontal scale) signals.

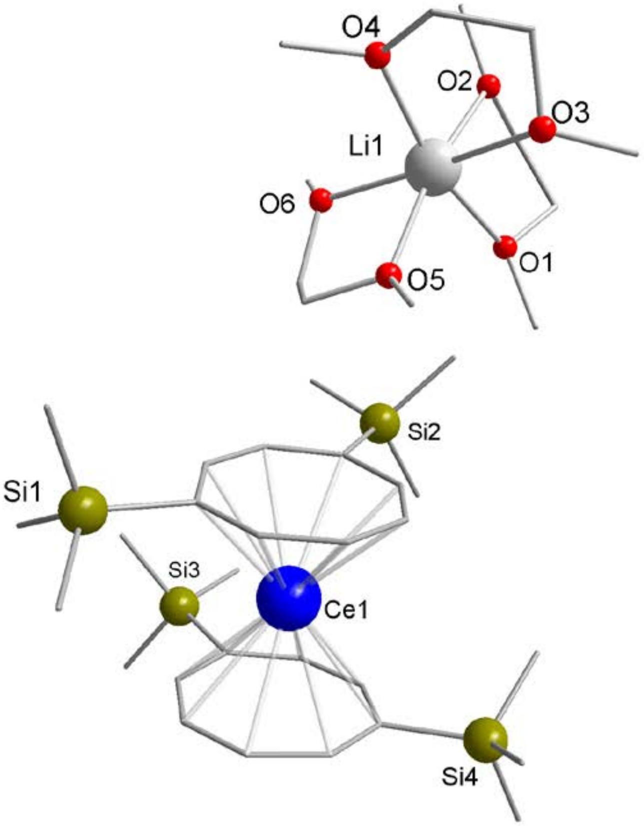


Fig. S3. Partially labled molecular X-ray structure of **1**, hydrogen atoms are omitted for clarity. Colour code: blue (Ce^{III}), green (Si), grey-wire (C), pale grey (Li), red (O).

Table S1. Selected Crystallographic data for **1.**

	1
Nearest Ce^{III} intermolecular distance (Å)	11.58(5)
Average M-COT''$_{centroid}$ (Å)	2.07(3)
Nearest Li-C$_{COT''}$ (Å)	5.72(1)
Average C$_{COT''}$-Ce^{III} distance (Å)	2.77(1)
Average Si-C$_{cot}$ (Å)	1.87(8)
M_r (g/mol)	914.44
Formula	$CeC_{40}H_{78}LiO_6Si_4$
T(K)	200(2)
γ (Å)	0.71073
Crystal system	triclinic
Space group	P -1 (2)
a (Å)	11.744(4)
b (Å)	12.376(4)
c (Å)	18.533(6)
α (deg)	99.150(7)°
β (deg)	102.147(7)°
γ (deg)	98.922(6)°
V (Å^3)	2549.75(688)
ρ_{calc} (cm^{-3})	1.191
Z	2
Reflections collected	33388
R(int)	13751, 0.0170
R1	0.0362
wR2	0.0757
Reflections with $I > 2\sigma(I)$	11109

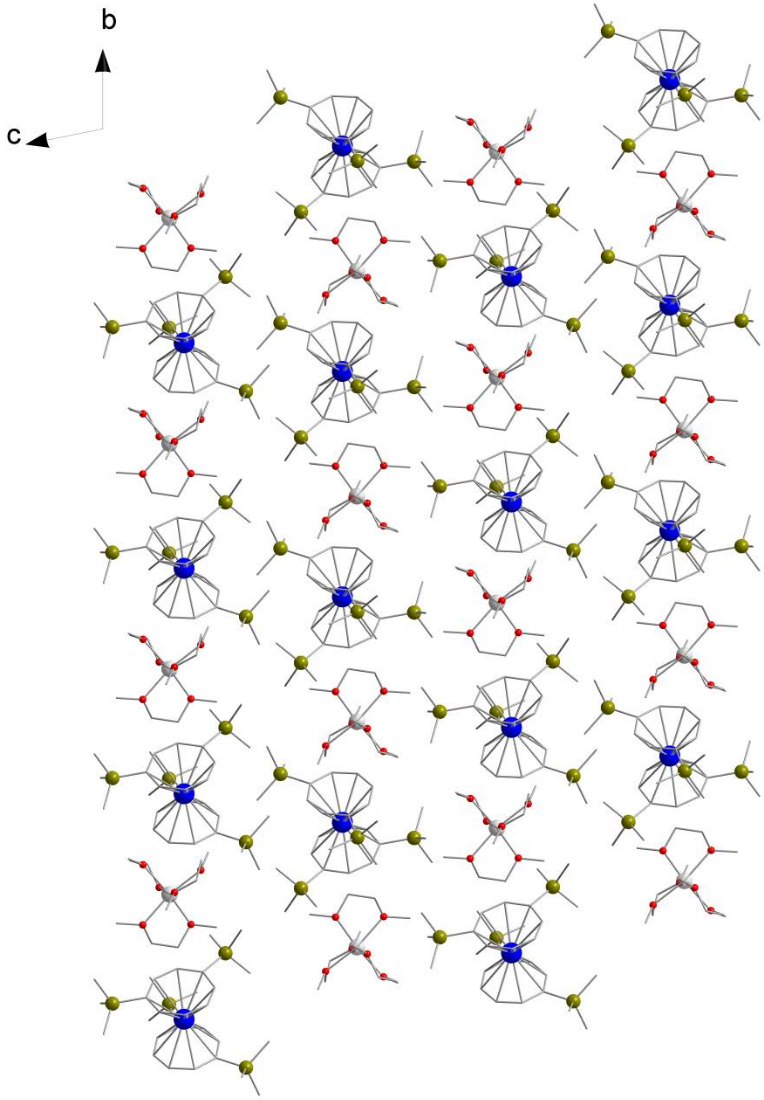


Fig. S4. Packing arrangement of **1** looking down the *a* axis. H atoms are omitted for clarity. Color code: Si = green, Ce^{III} = blue, Li = pale grey, O = red, C = grey-wire.

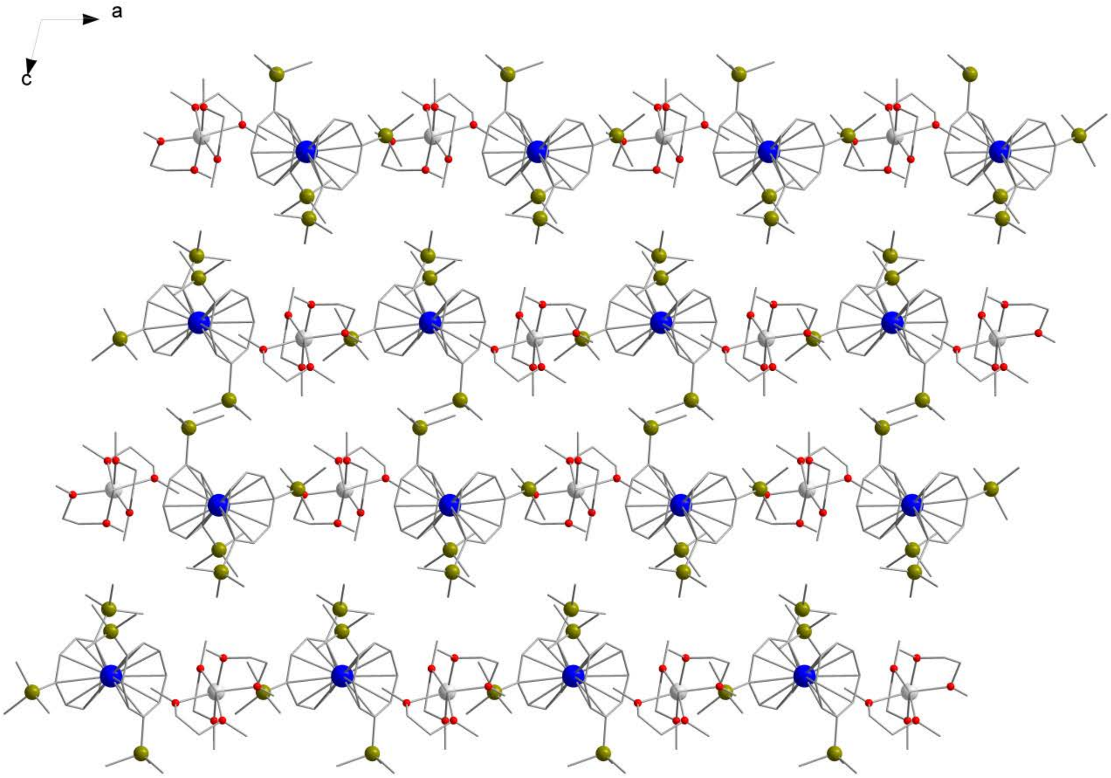


Fig. S5. Packing arrangement of **1** looking down the *b* axis. H atoms are omitted for clarity. Color code: Si = green, Ce^{III} = blue, Li = pale-grey, O = red, C = grey-wire.

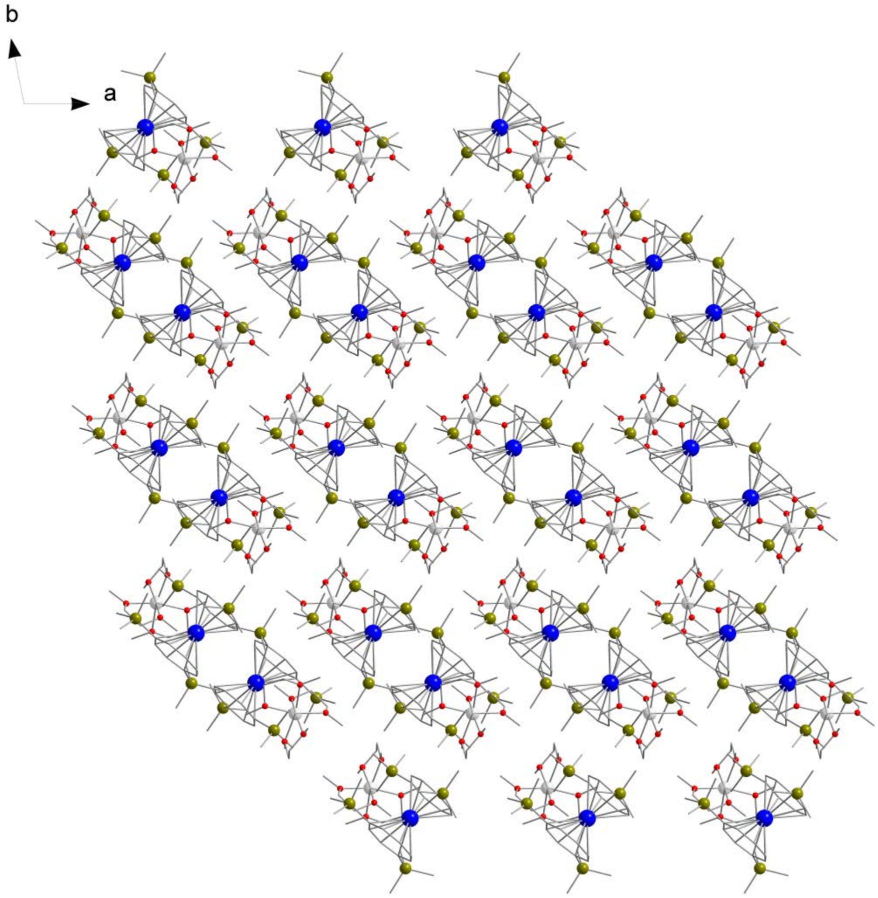


Fig. S6. Packing arrangement of **1** looking down the *c* axis. H atoms are omitted for clarity. Color code: Si = green, Ce^{III} = blue, Li = pale-grey, O = red, C = grey-wire.

Table S2. Electrochemical analysis of **1**.

Scan rate (V/s)	sqrt. Scan rate	E_{pa} (V)	I_{pa} (A)	E_{pc} (V)	I_{pc} (A)
1.00	1.00	-1.36	-1.11E-05	-1.49	8.29E-06
0.50	0.707	-1.37	-7.67E-06	-1.49	6.69E-06
0.25	0.500	-1.38	-5.68E-06	-1.48	5.51E-06
0.10	0.316	-1.39	-3.90E-06	-1.47	3.93E-06
0.05	0.224	-1.39	-2.99E-06	-1.47	2.94E-06

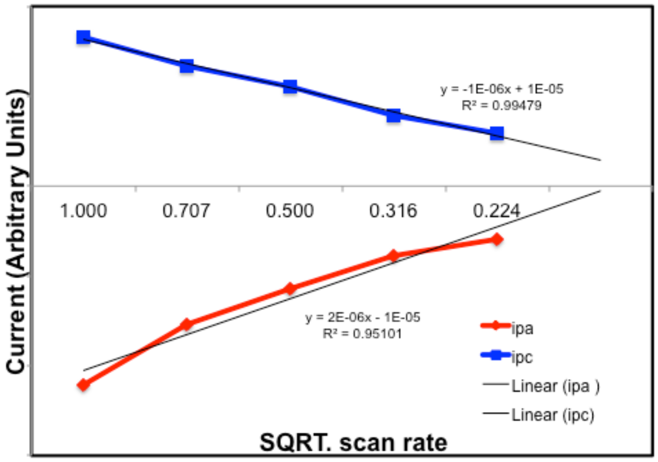


Fig. S7. Randels–Sevcik plot of cyclic voltammogram data.

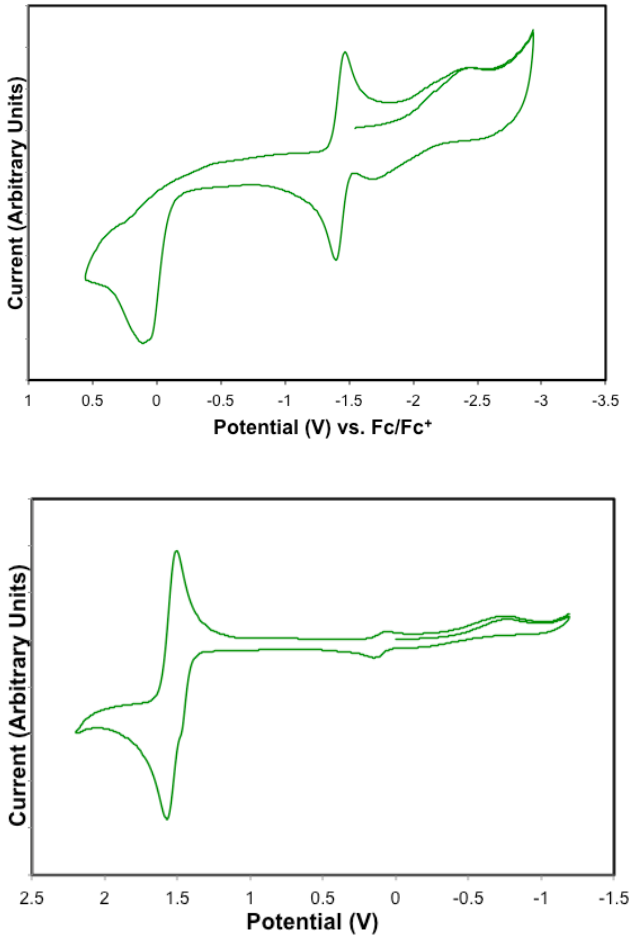


Fig. S8. (Top) Cyclic Voltammograms for **1** showing a potential window from +0.60 V to –3.00 V. (Bottom) Cyclic Voltammograms for **1** with ferrocene internal standard in a potential window from +2.20 V to –1.20 V (scan rate = 100 mV/s for both).

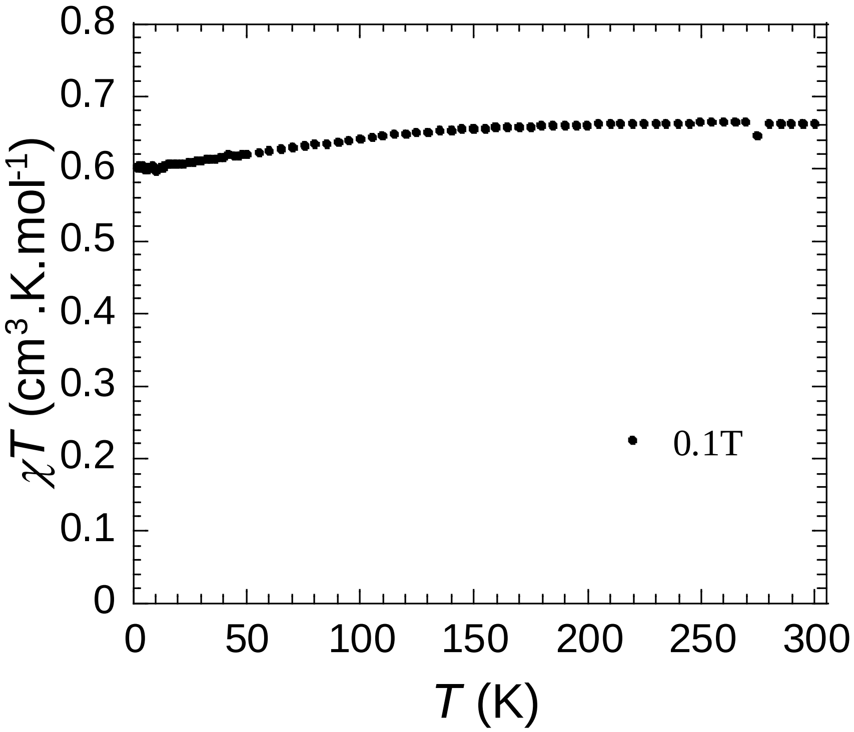


Fig. S9. Temperature dependence of the χT product under 0.1 T for complex **1**, with χ being the molar susceptibility per molecule defined as M/H.

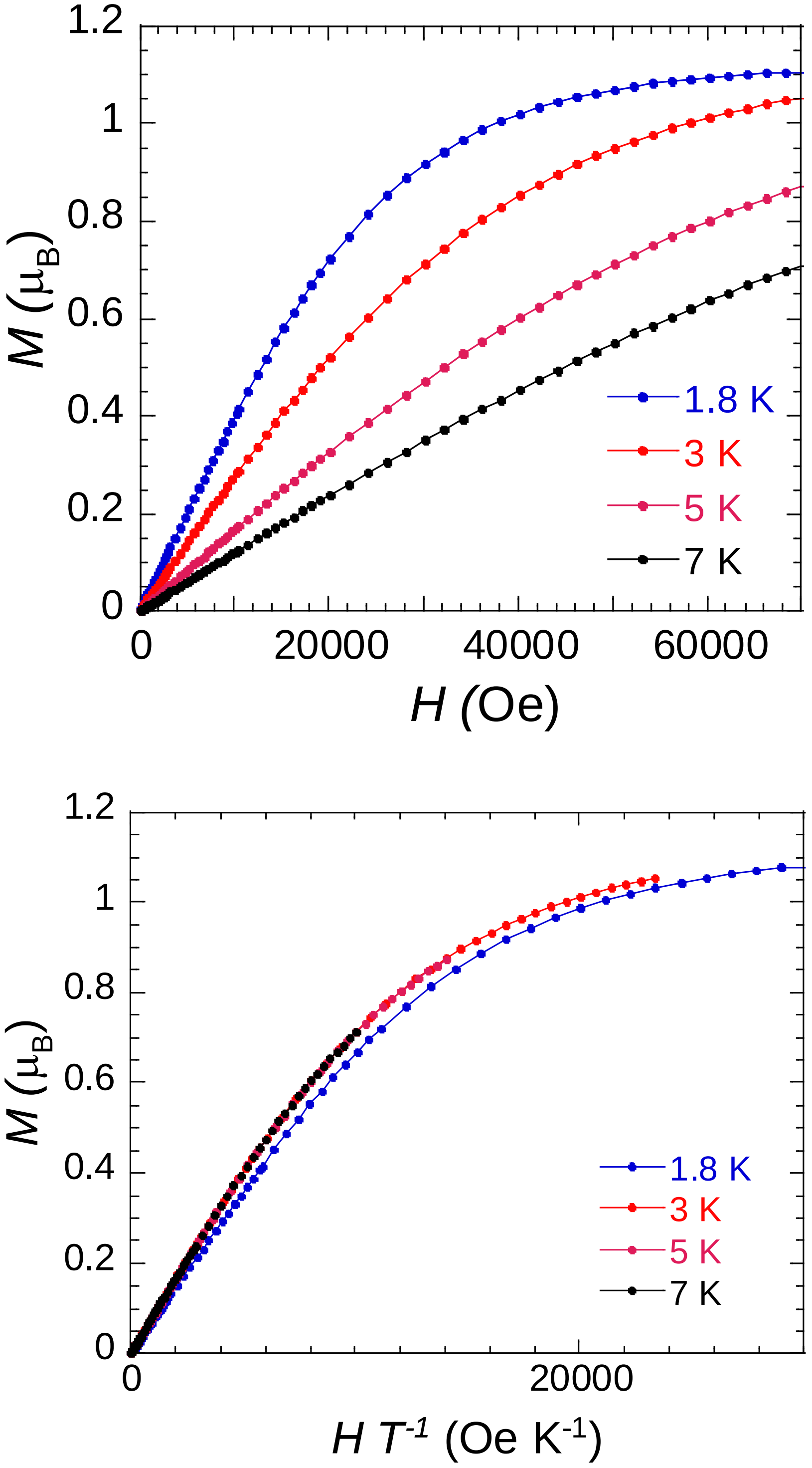
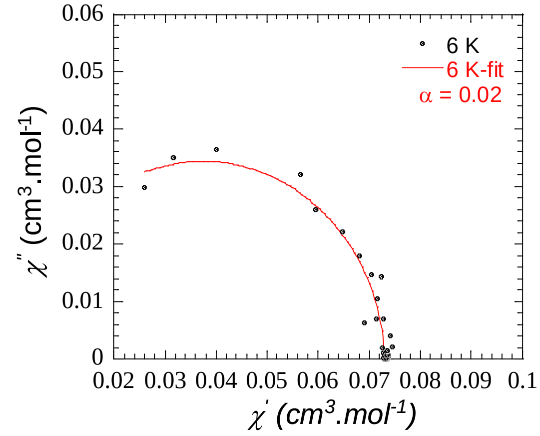
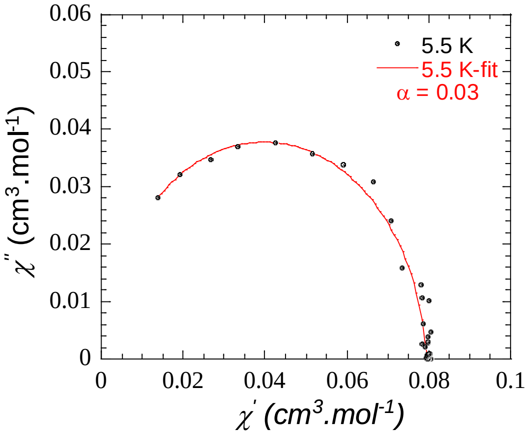
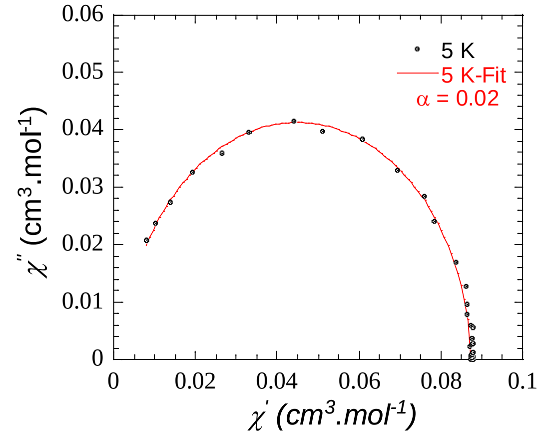
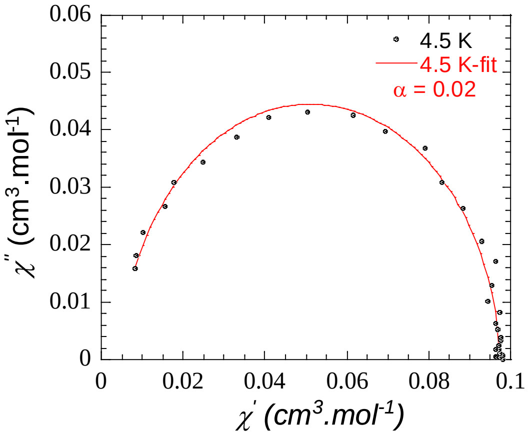


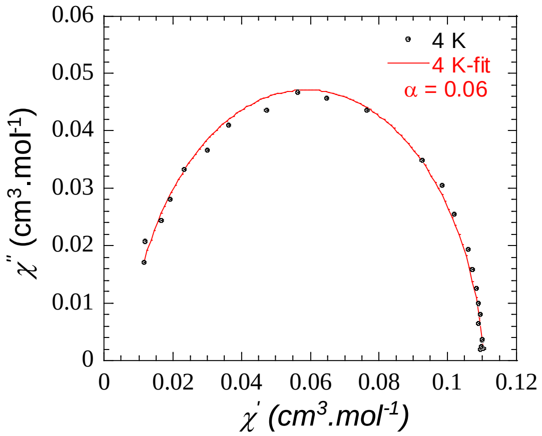
Figure S10: Field dependence of the magnetization (top) and reduced magnetization (bottom) for **1** at 1.8, 3, 5, and 7 K.

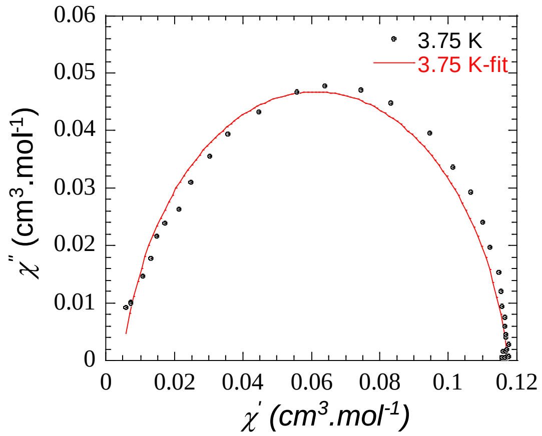

6 K
6 K-fit
α = 0.02
χ'' (cm^3.mol^{-1})
χ' (cm^3.mol^{-1})
0
0.01
0.02
0.03
0.04
0.05
0.06
0.02
0.03
0.04
0.05
0.06
0.07
0.08
0.09
0.1

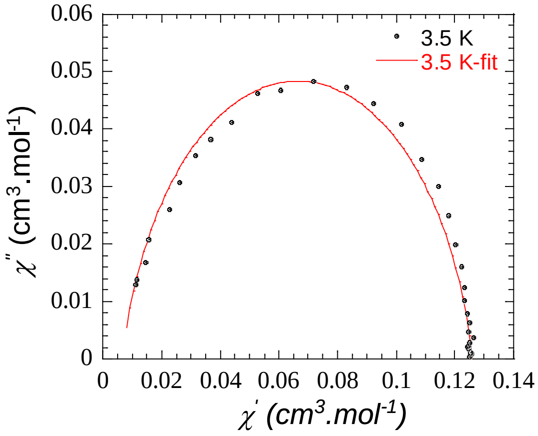

5.5 K
5.5 K-fit
α = 0.03
χ'' (cm^3.mol^{-1})
χ' (cm^3.mol^{-1})
0
0.01
0.02
0.03
0.04
0.05
0.06
0
0.02
0.04
0.06
0.08
0.1

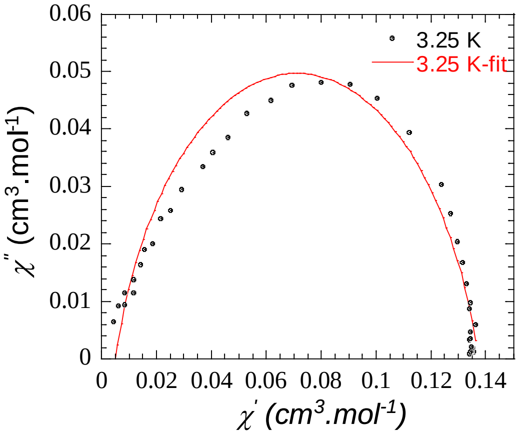

5 K
5 K-Fit
α = 0.02
χ'' (cm^3.mol^{-1})
χ' (cm^3.mol^{-1})
0
0.01
0.02
0.03
0.04
0.05
0.06
0
0.02
0.04
0.06
0.08
0.1

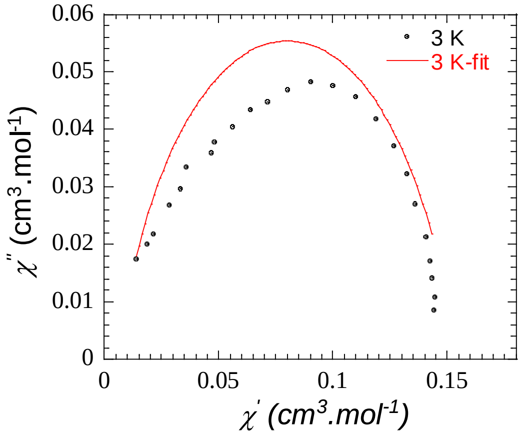

4.5 K
4.5 K-fit
α = 0.02
χ'' (cm^3.mol^{-1})
χ' (cm^3.mol^{-1})
0
0.01
0.02
0.03
0.04
0.05
0.06
0
0.02
0.04
0.06
0.08
0.1

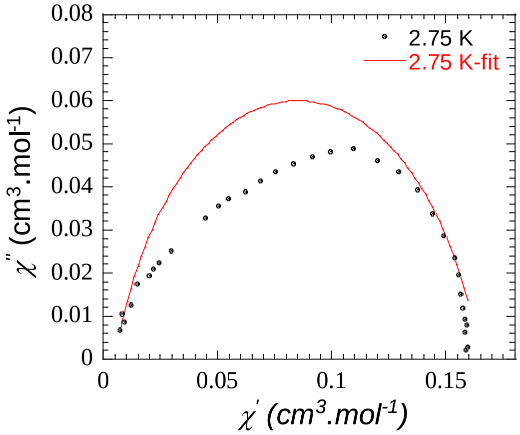

4 K
4 K-fit
α = 0.06
χ'' (cm^3.mol^{-1})
χ' (cm^3.mol^{-1})
0
0.01
0.02
0.03
0.04
0.05
0.06
0
0.02
0.04
0.06
0.08
0.1
0.12

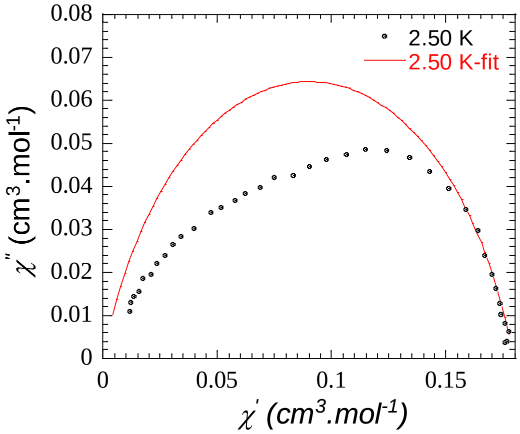

3.75 K
3.75 K-fit
χ'' (cm^3.mol^{-1})
χ' (cm^3.mol^{-1})
0
0.01
0.02
0.03
0.04
0.05
0.06
0
0.02
0.04
0.06
0.08
0.1
0.12

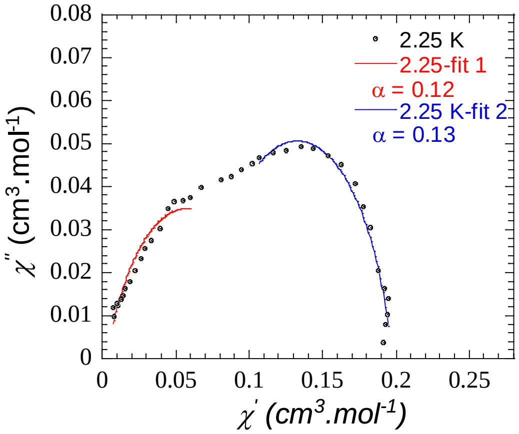

3.5 K
3.5 K-fit
χ'' (cm^3.mol^{-1})
χ' (cm^3.mol^{-1})
0
0.01
0.02
0.03
0.04
0.05
0.06
0.02
0.04
0.06
0.08
0.1
0.12
0.14


3.25 K
3.25 K-fit
χ'' (cm^3.mol^{-1})
χ' (cm^3.mol^{-1})
0
0.01
0.02
0.03
0.04
0.05
0.06
0.02
0.04
0.06
0.08
0.1
0.12
0.14


3 K
3 K-fit
χ'' (cm^3.mol^{-1})
χ' (cm^3.mol^{-1})
0
0.01
0.02
0.03
0.04
0.05
0.06
0.05
0.1
0.15


2.75 K
2.75 K-fit
χ'' (cm^3.mol^{-1})
χ' (cm^3.mol^{-1})
0
0.01
0.02
0.03
0.04
0.05
0.06
0.07
0.08
0.05
0.1
0.15


2.50 K
2.50 K-fit
χ'' (cm^3.mol^{-1})
χ' (cm^3.mol^{-1})
0
0.01
0.02
0.03
0.04
0.05
0.06
0.07
0.08
0.05
0.1
0.15


2.25 K
2.25-fit 1
α = 0.12
2.25 K-fit 2
α = 0.13
χ'' (cm^3.mol^{-1})
χ' (cm^3.mol^{-1})
0
0.01
0.02
0.03
0.04
0.05
0.06
0.07
0.08
0.05
0.1
0.15
0.2
0.25

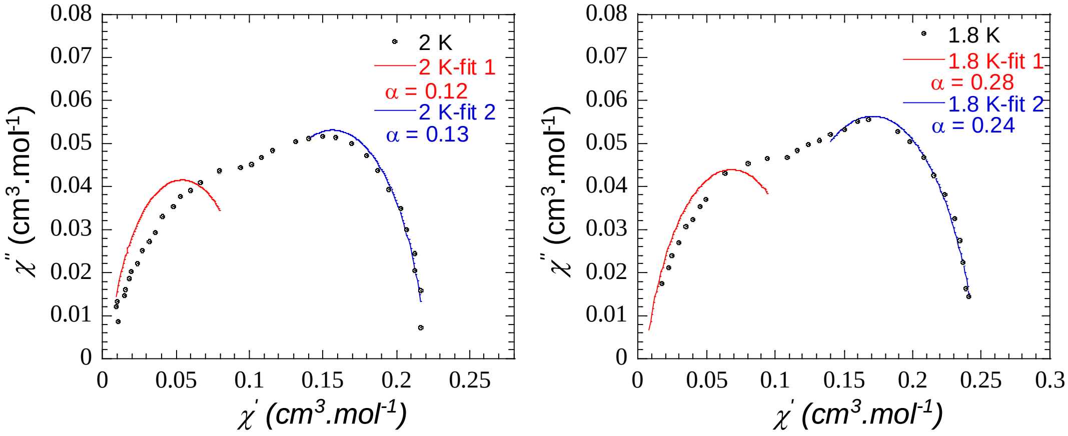


Fig S11. *Cole-Cole* plot for ac susceptibility data of **1** under a 400 Oe applied dc field, solid lines correspond to the fit.

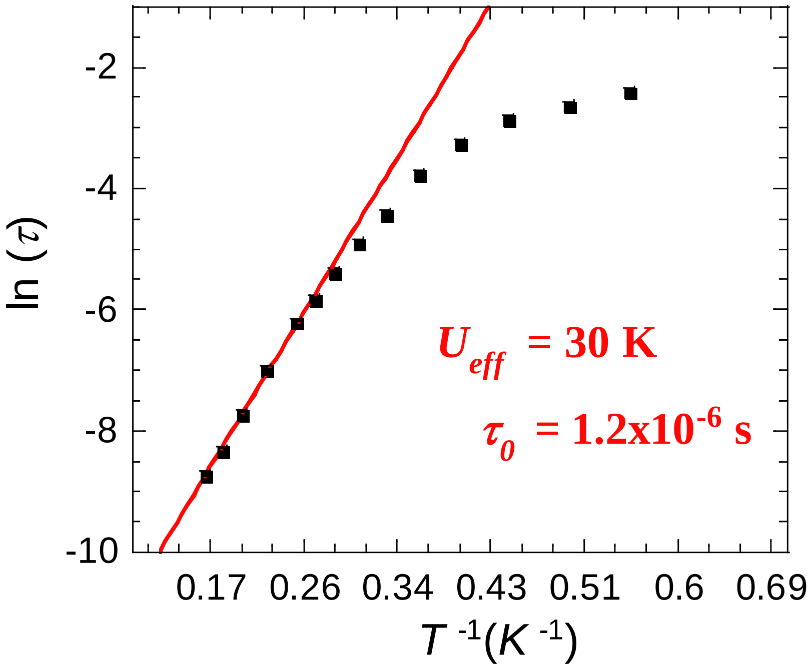


Fig. S12: Relaxation time of the magnetization ln(τ) *vs*. T^{-1} for **1** (Arrhenius plot using ac data) under 400 Oe applied field. The solid line corresponds to the fit.