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Supporting information for

Ligand effects on the magnetic anisotropy of tetrahedral cobalt complexes

Mohamed R. Saber,[a,b] *and Kim R. Dunbar*[a]*

a Department of Chemistry, TexasA&M University, College Station, Texas77842-3012
E-mail: dunbar@mail.chem.tamu.edu

b Department of Chemistry, Fayoum University, Fayoum, 63514, Egypt.

RECEIVED DATE (automatically inserted by publisher); E-mail: dunbar@mail.chem.tamu.edu

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Experimental Section
Syntheses

All complexes were synthesized following previously reported procedures.[1]

Co(quinolone)$_2$I$_2$ (1). A solution of quinoline (416 mg, 3.22 mmol) in 10 mL of hot anhydrous ethanol was added to a hot solution of CoI_2 (500 mg, 1.6 mmol) in the same solvent. The blue green reaction was refluxed for 1 hour and cooled in air. The X ray quality blue green crystals that grew in the solution were collected by filtration and washed with 3 mL of cold ethanol followed by 3 mL of diethyl ether and finally dried under vacuum (Yield = 0.46 g, 51%).

Co(PPh$_3$)$_2$I$_2$ (2). A solution of PPh_3 (840 mg, 3.2 mmol) in 10 mL of hot anhydrous ethanol was added to a hot solution of CoI_2 (500 mg, 1.6 mmole) in the same solvent. Reddish brown crystals of the product formed instantaneously. The reaction was refluxed for 1 hour and then cooled in air. The resulting X ray quality crystals were collected by filtration, washed with 3 mL of cold ethanol followed by 3 mL of diethyl ether and then dried under vacuum (Yield = 1.0 g, 75%).

Co(AsPh$_3$)$_2$I$_2$ (3). A solution of $AsPh_3$ (1000 mg, 3.26 mmol) in 10 mL of hot anhydrous nitromethane was added to a hot solution of CoI_2 (550 mg, 1.75 mmol) in the same solvent. Yellow brown crystals of the product deposited instantly. The reaction was refluxed for 1 hour and then left to cool for three hours. X-ray quality crystals were collected by filtration, washed with cold nitromethane followed by 3 mL of diethyl ether and then dried under vacuum (Yield = 1.35 g, 83%).

X-ray Crystallographic Measurements

X-ray diffraction data for **1-3** were collected at 110 K on a Bruker Apex II diffractometer equipped with a CCD area detector and Mo$K\alpha$ radiation. Absorption corrections were applied by using SADABS.[2] All structures were solved by direct methods (SHELXS-97)[3] and refined by full-matrix least-squares calculations on F^2 (SHELXL-97).[4] The non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined isotropically. Table S1 provides a summary for the crystal parameters and refined structures data.
CCDC- 1003633-1003635 contain the supplementary crystallographic data for this paper. These can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

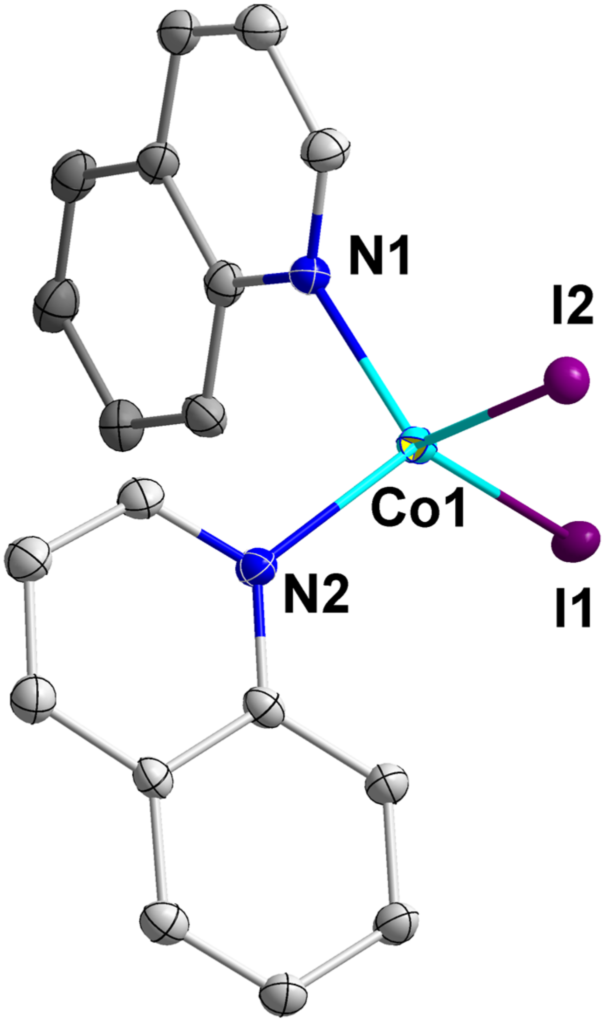
Table S 1. Crystal data and details of the refinement parameters for compounds $(Ph_3PMe)_2[Fe_2(TCNQ)_3]$ **1,** $(Ph_3PMe)_2[Co_2(TCNQ)_3]$ **2,** $(Ph_3PMe)_2[Ni_2(TCNQ)_3]$ **3**, and $(Ph_3PMe)_2[Zn_2(TCNQ)_3]$ **4.**

Compound	**1**	**2**	**3**
Formula	$C_{18}\,H_{14}\,Co\,I_2\,N_2$	$C_{36}\,H_{30}\,Co\,I_2\,P_2$	$C_{36}\,H_{30}\,Co\,I_2\,As_2$
F_w [g mol^{-1}]	571.04	837.27	925.17
Crystal size [mm^3]	0.04 x 0.04 x 0.18	0.05 x 0.1 x 0.16	0.08 x 0.24 x 0.29
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/c$
a [Å]	7.9139(16)	19.165(4)	19.117(4)
b [Å]	15.284(3)	10.198(2)	10.215(2)
c [Å]	14.611(3)	17.929(4)	18.245(4)
α[°]	90.00	90.00	90.00
β [°]	90.99(3)	112.23(3)	111.72(3)
γ[°]	90.00	90.00	90.00
V [Å^3]	1766.9(6)	3243.7(11)	3309.9(11)
Z	4	4	4
ρ_{calc} [g cm^{-3}]	2.147	1.715	1.857
μ (MoKα) [mm^{-1}]	4.465	2.555	4.392
Reflections collected	20501	37469	36835
Independent reflections	4072	7504	7480
Parameters	208	370	370
R(int)	0.0255	0.0236	0.0355
$R1$[a]	0.0255	0.0291	0.0395
$wR2$[b]	0.056	0.0562	0.0839
GOF	1.046	1.026	1.055

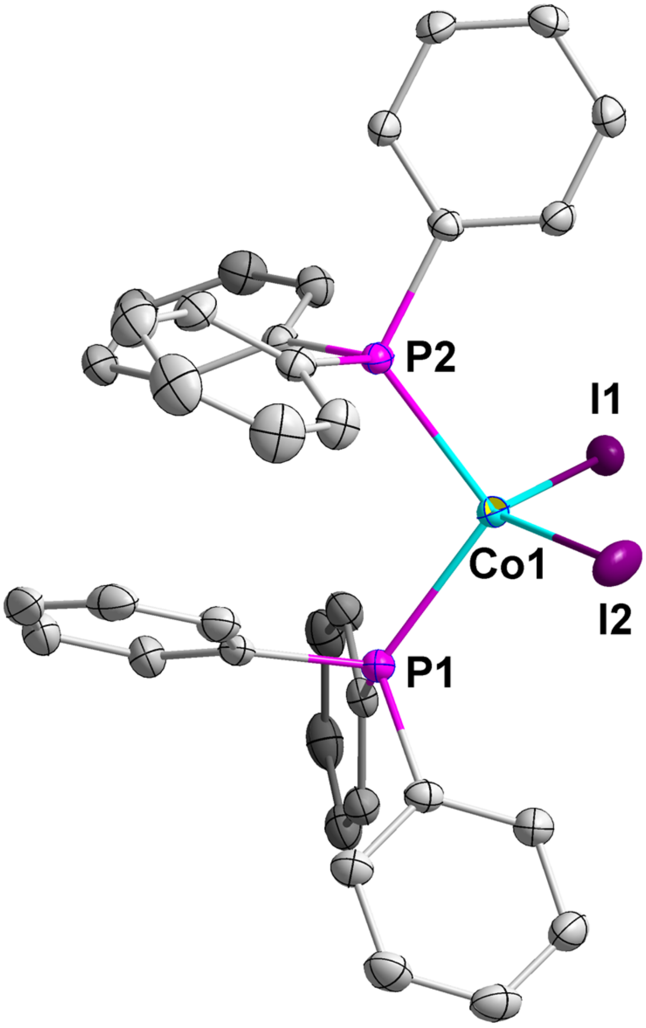
[a] $R1 = \Sigma||F_o| /|F_c||\Sigma|F_o|$. [b] $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$

Table S 2. Bond distances and angles for **1-3**.

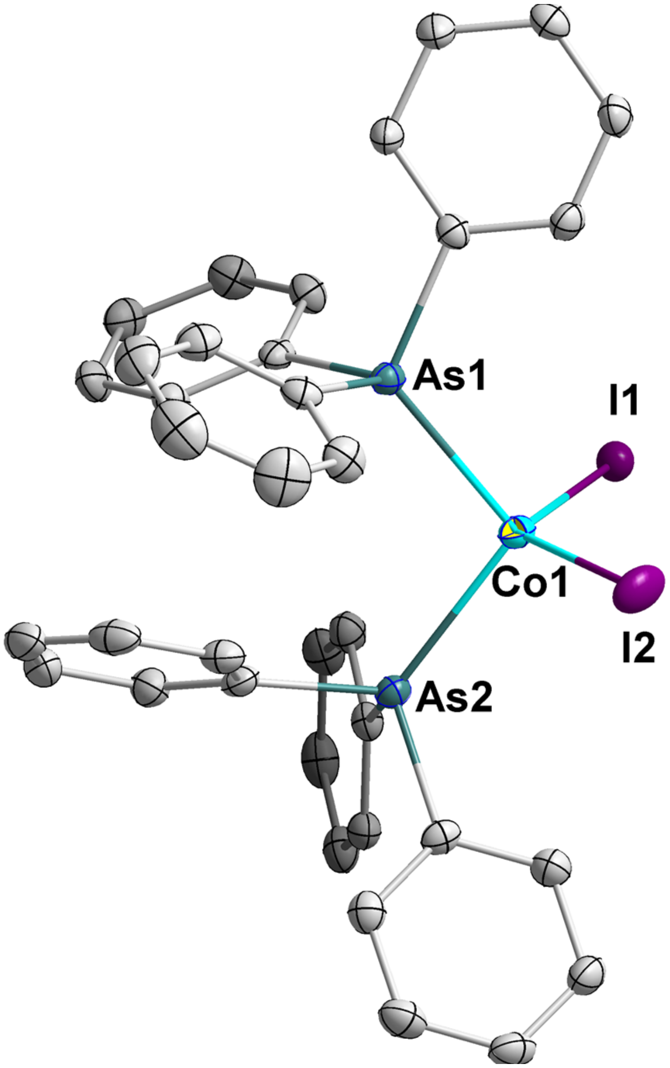
Selected bond distances (Å) and angles for (**1**)						
Co1	I1	2.5803(7)	I1	Co1	I2	109.72(2)
Co1	I2	2.5770(7)	I1	Co1	N1	108.51(7)
Co1	N1	2.053(3)	I1	Co1	N2	119.59(7)
Co1	N2	2.057(3)	I2	Co1	N1	111.64(7)
			I2	Co1	N2	105.38(7)
			N1	Co1	N2	101.8(1)
Selected bond distances (Å) and angles for (**2**)						
I1	Co1	2.5433(7)	I1	Co1	I2	111.44(1)
I2	Co1	2.5580(5)	I1	Co1	P2	105.39(2)
Co1	P2	2.3899(7)	I1	Co1	P1	109.04(2)
Co1	P1	2.4129(8)	I2	Co1	P2	112.71(2)
			I2	Co1	P1	109.84(2)
			P2	Co1	P1	108.25(2)
Selected bond distances (Å) and angles for (**3**)						
Co1	I1	2.5273(9)	I1	Co1	I2	116.80(2)
Co1	I2	2.5303(8)	I1	Co1	As1	108.44(2)
Co1	As1	2.5137(9)	I1	Co1	As2	104.23(2)
Co1	As2	2.4826(8)	I2	Co1	As1	109.73(2)
			I2	Co1	As2	111.75(2)
			As1	Co1	As2	105.15(2)



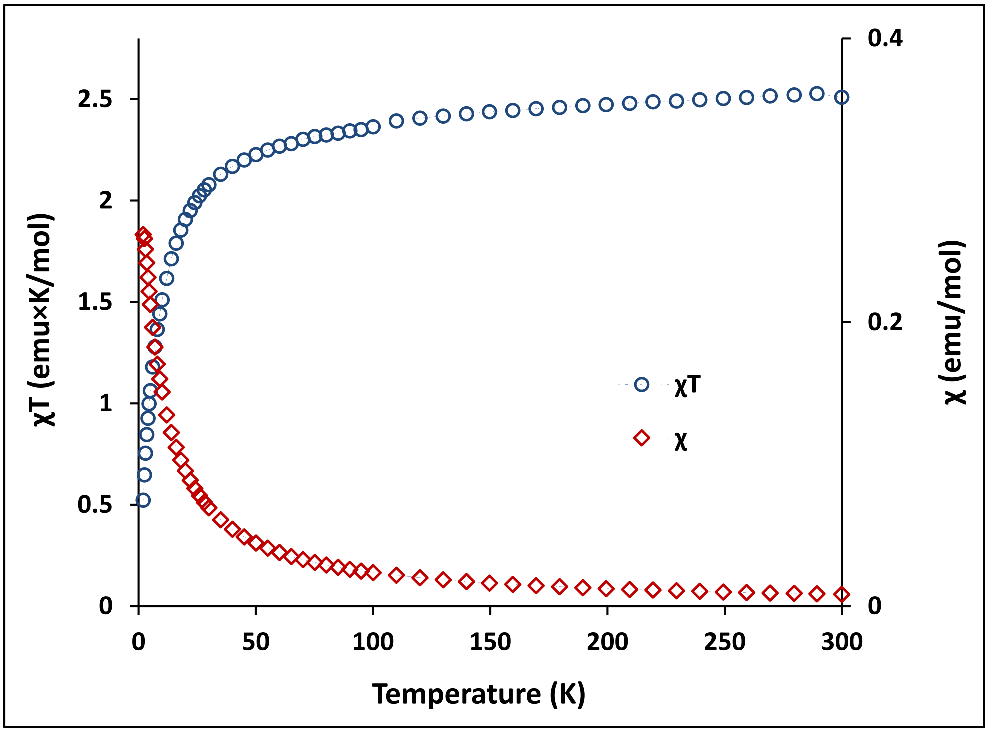
S 1. Thermal ellipsoid plot of **1**



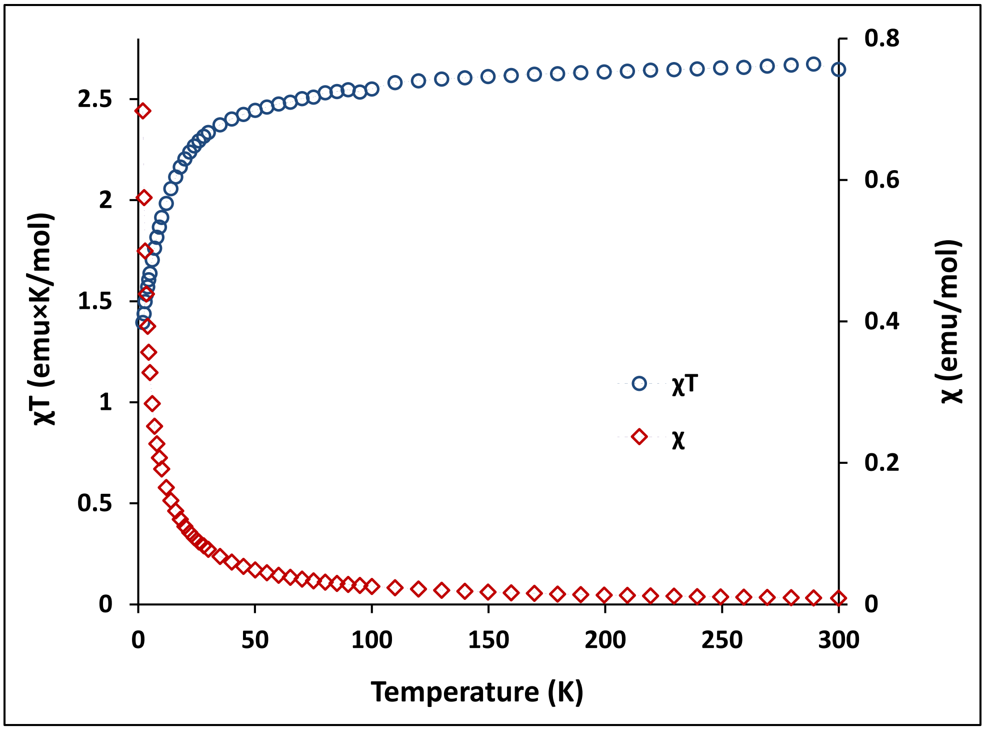
S 2. Thermal ellipsoid plot of **2**



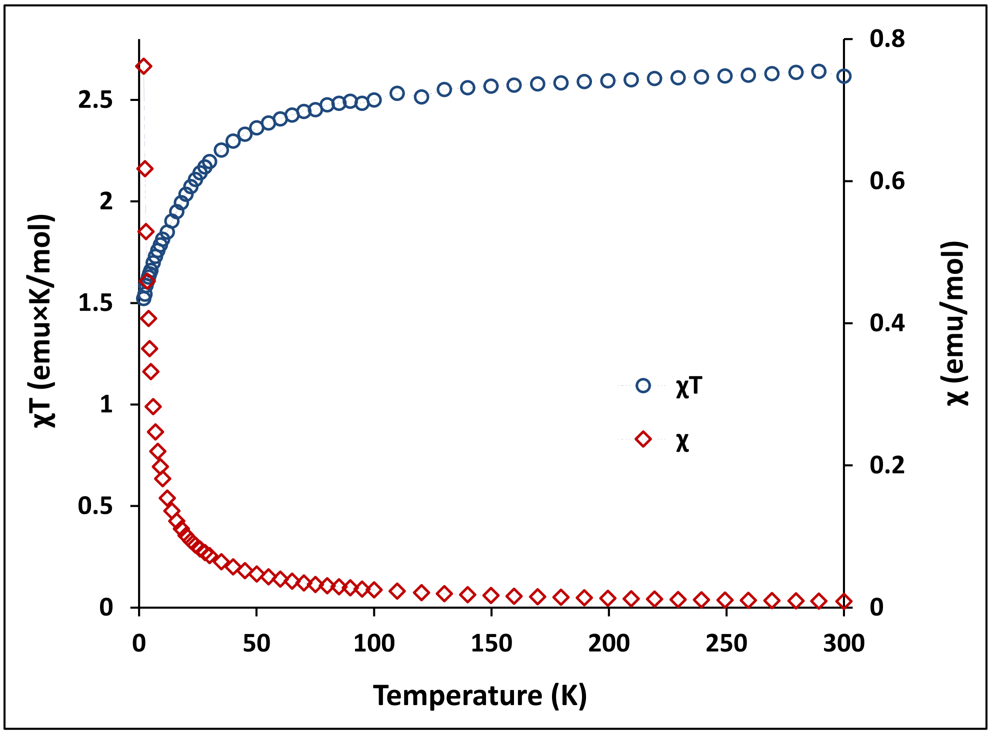
S 3. Thermal ellipsoid plot of **3**



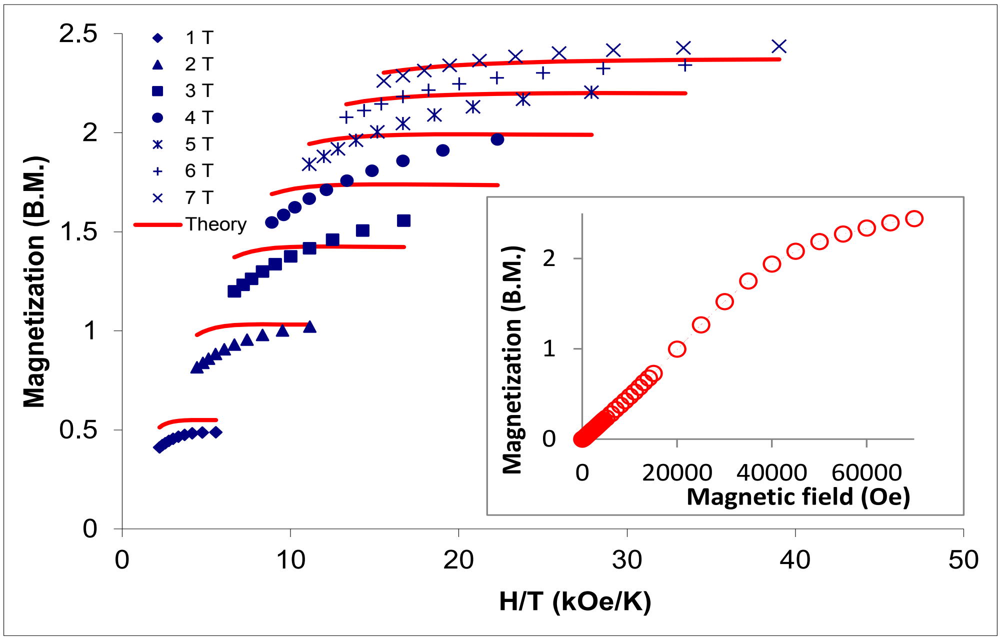
S 4. Variable temperature DC magnetic susceptibility data for **1**.



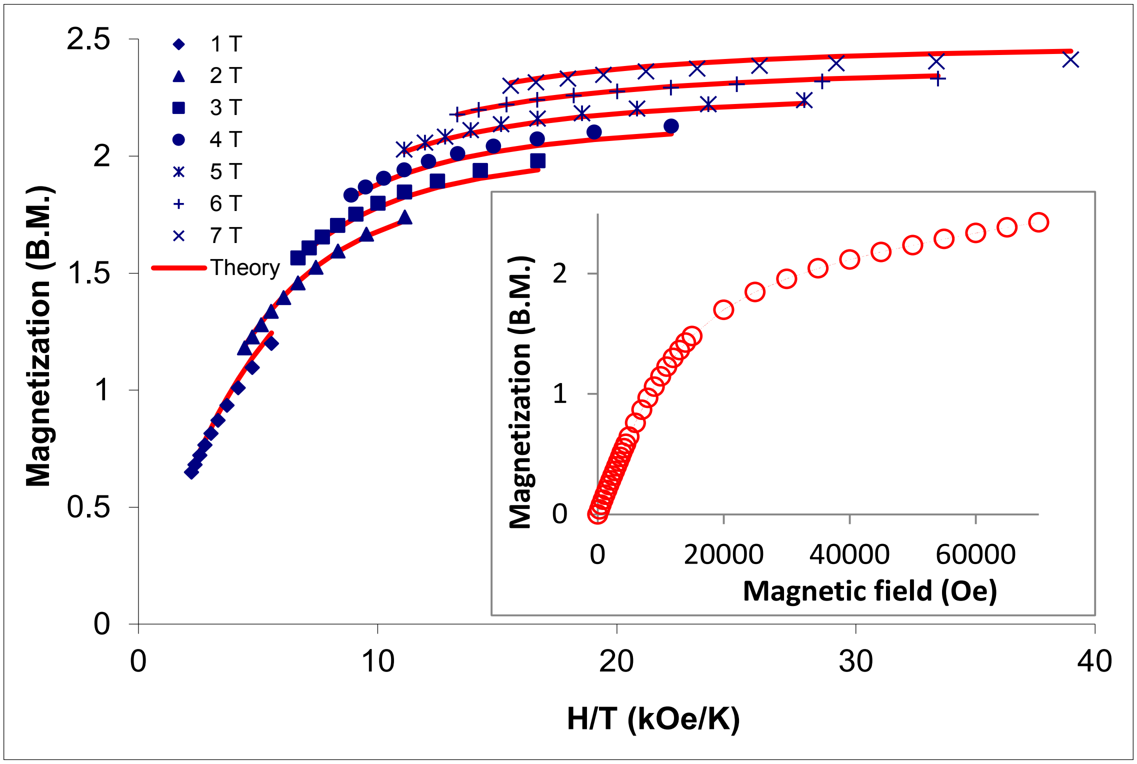
S 5. Variable temperature DC magnetic susceptibility data for **2**.



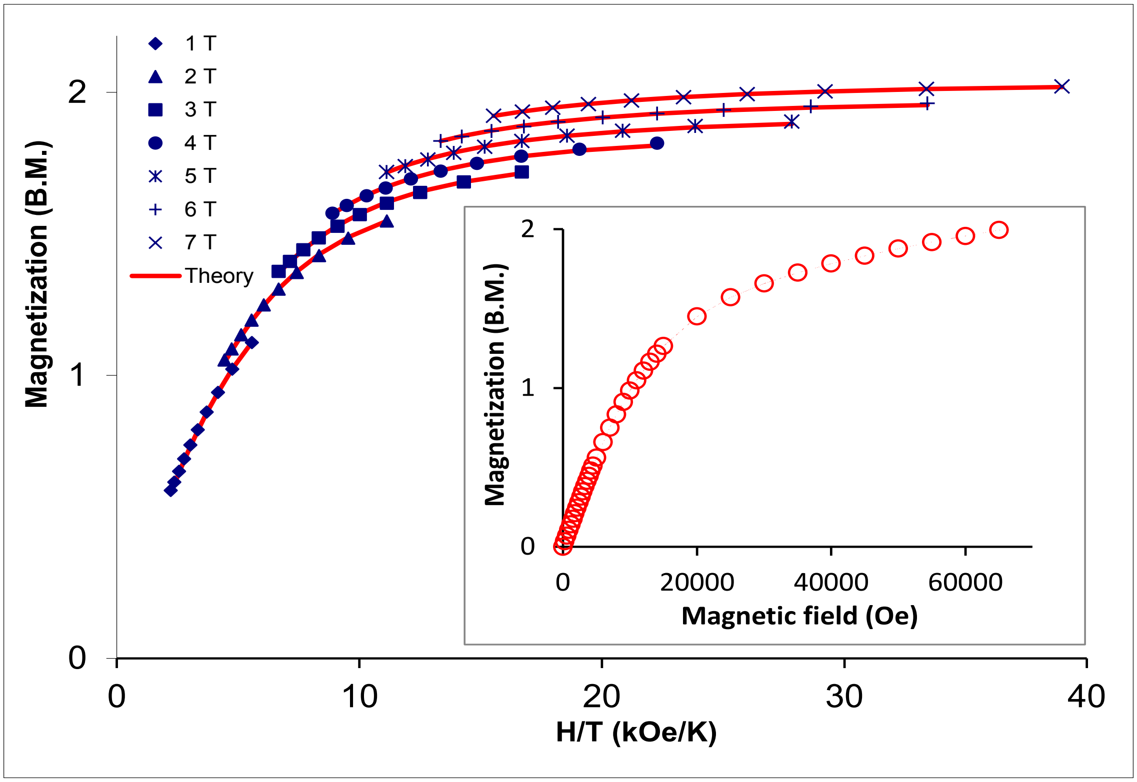
S 6. Variable temperature DC magnetic susceptibility data for **3**.



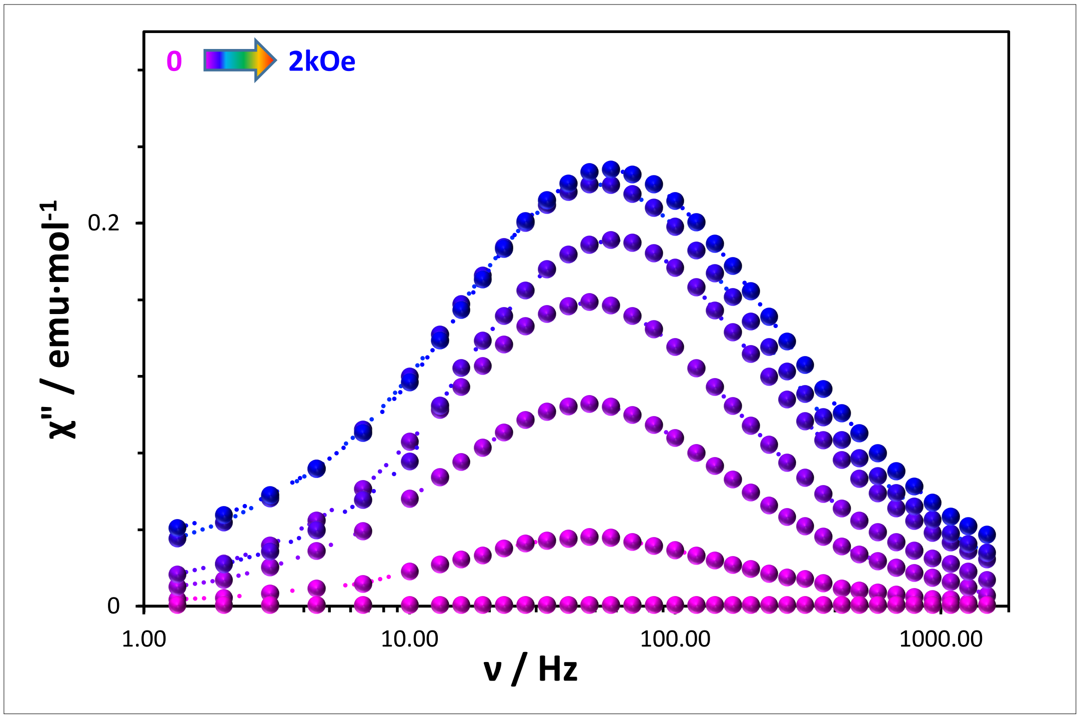
S 7. Reduced magnetization data for **1**. Inset; field dependent magnetization data at 1.8 K.

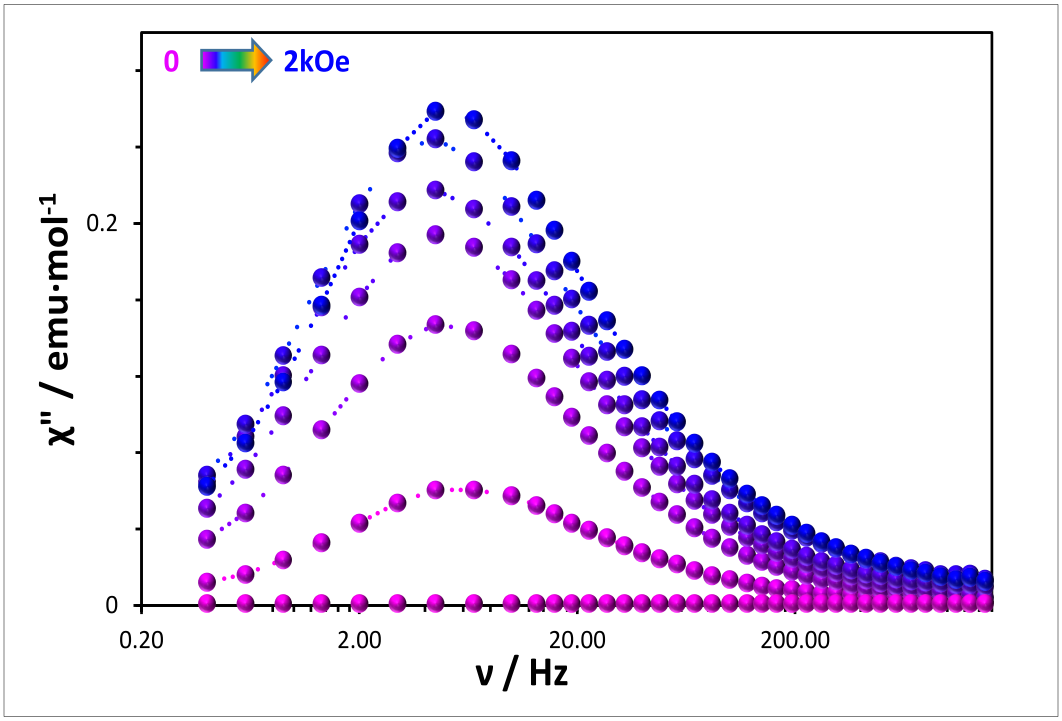


S 8. Reduced magnetization data for **2.** Inset; field dependent magnetization data at 1.8 K.

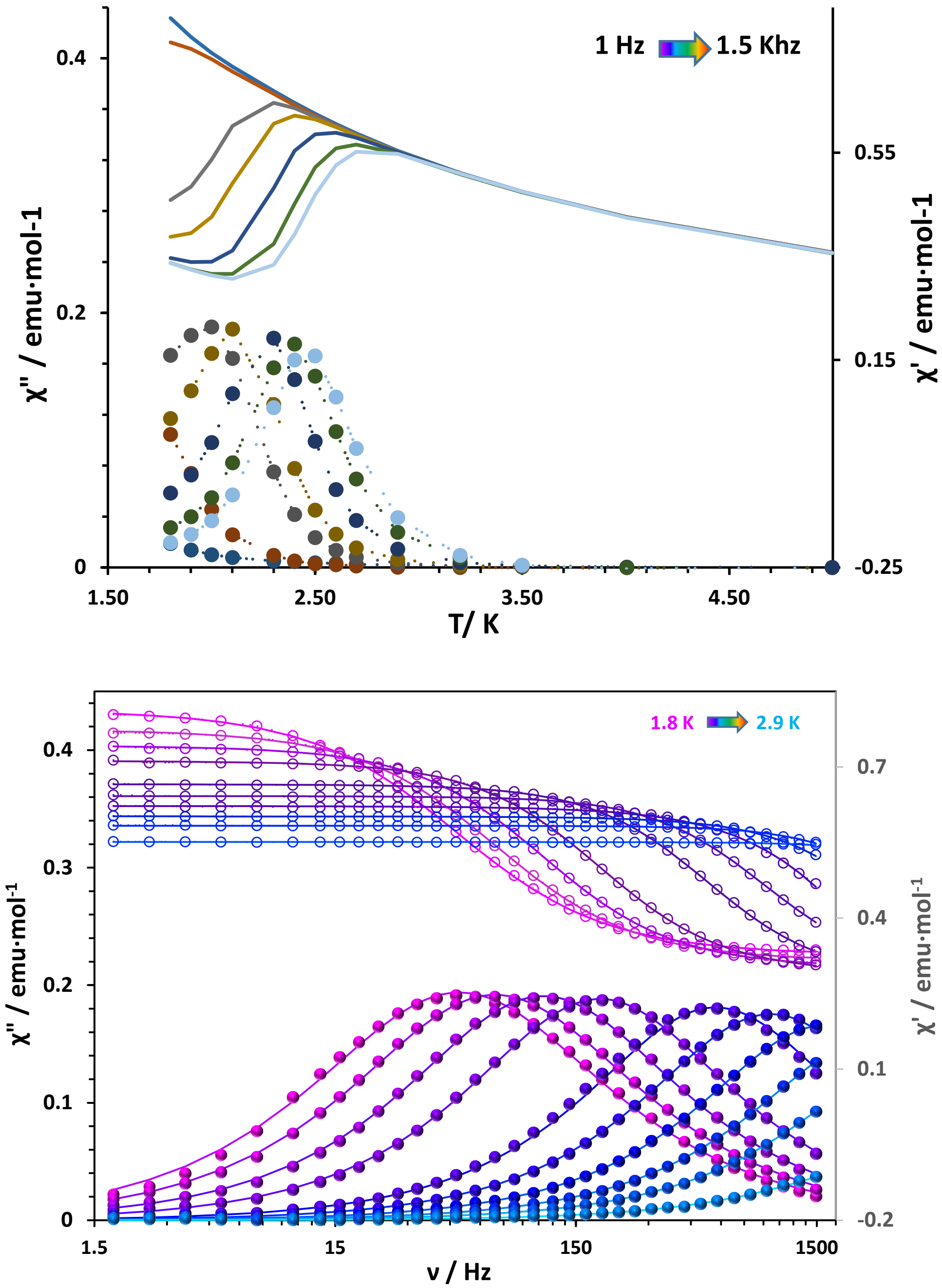


S 9. Reduced magnetization data for **3**. Inset; field dependent magnetization data at 1.8 K.

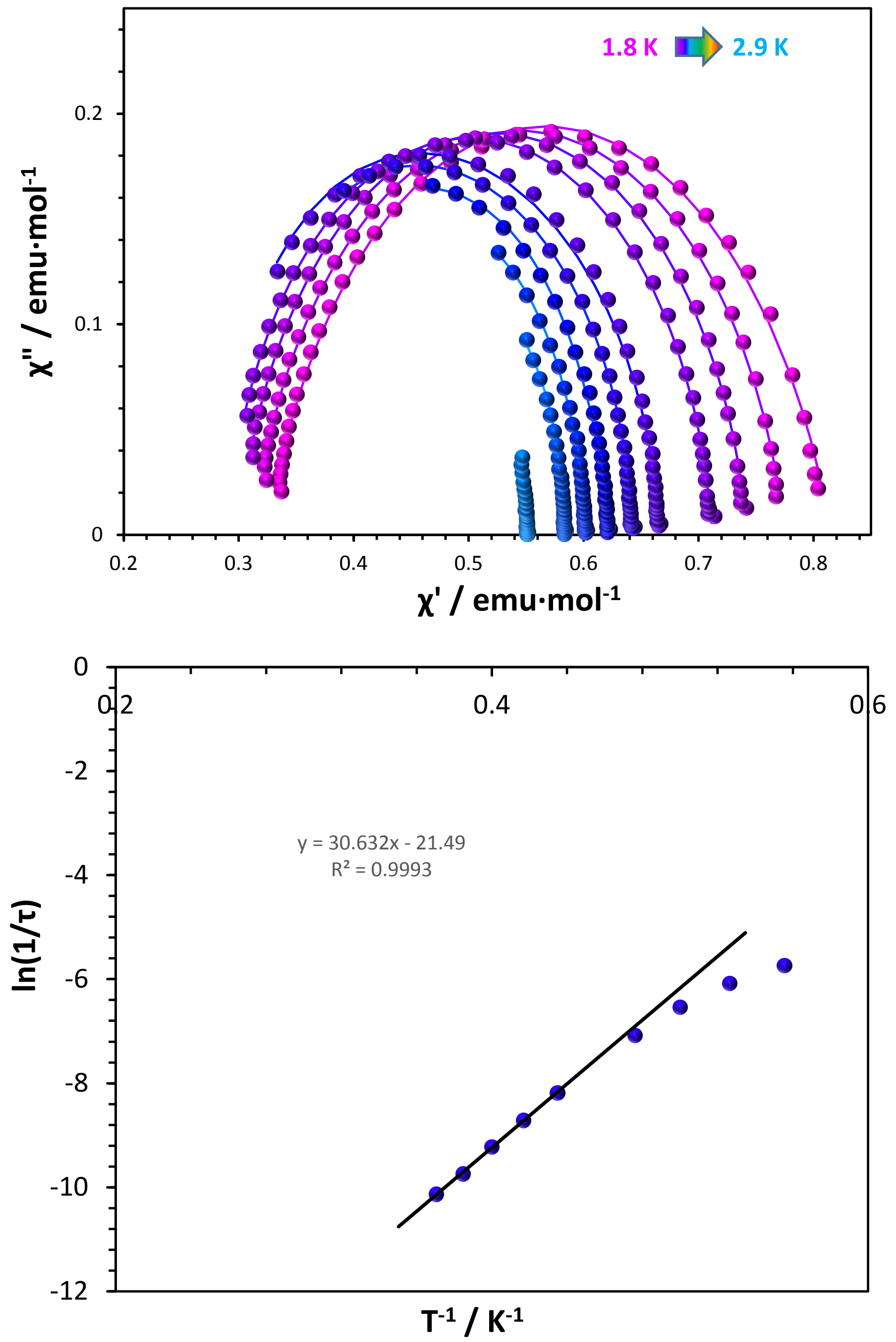




S 10. Fequency dependent AC measurements at different fields for **2** (top) **3** (bottom). Optimum field is 1000 Oe.



S 11. Temperature (top) and frequency (bottom) dependence of the AC susceptibility for **2**. In-phase (open) out-of-phase (solid).



S 12. Cole-Cole plots (top) and Arrhenius plot (bottom) for **2** with U_{eff} = 30.63 K, $\tau_{\circ}$ = 4.65x10^{-10} s

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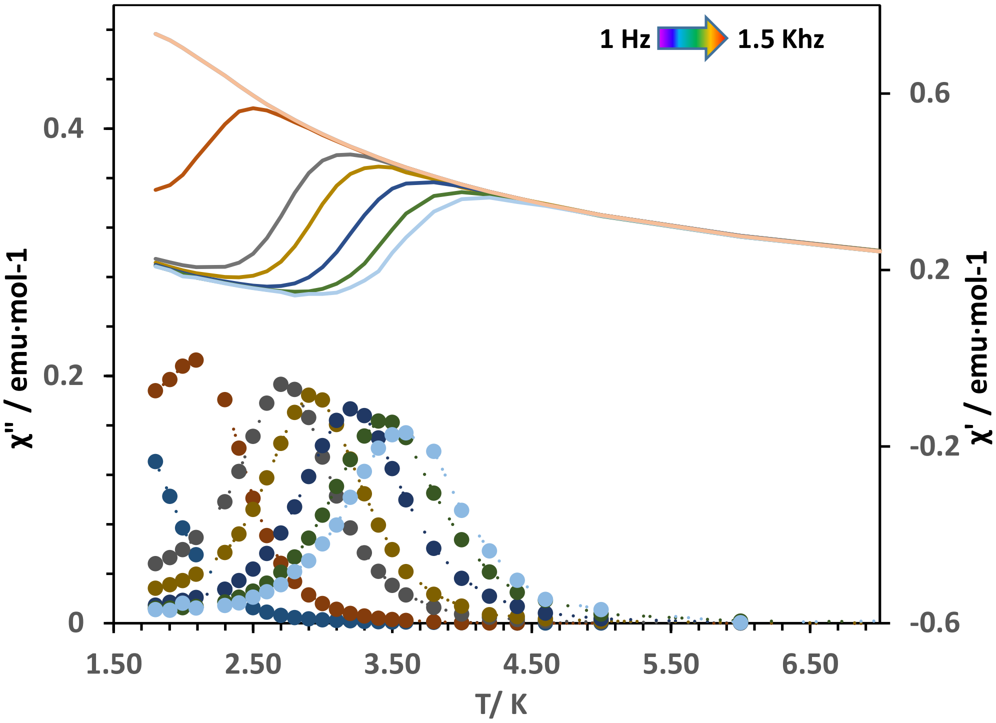
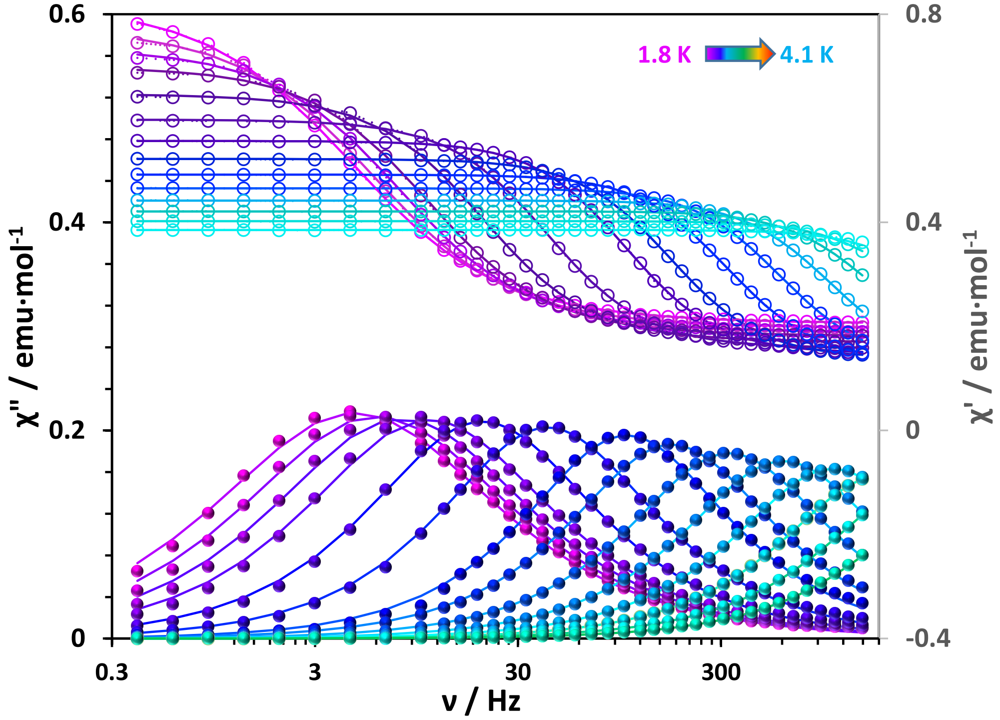
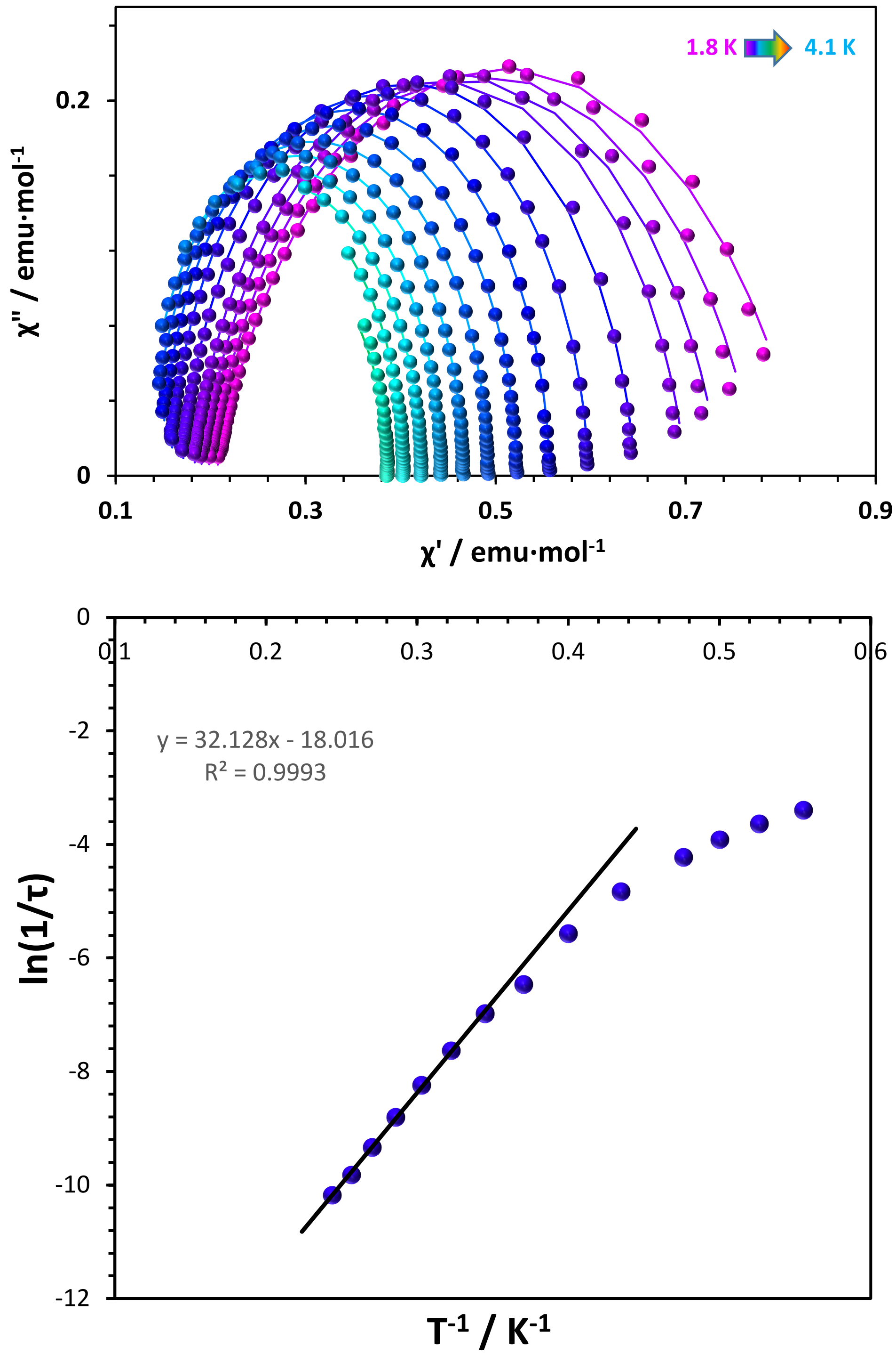




S 13. Temperature (top) and frequency (bottom) dependence of the AC susceptibility for **3**. In-phase (open) out-of-phase (solid).



S 14. Cole-Cole plots (top) and Arrhenius plot (bottom) for **3** with U_{eff}= 32.13 K, $\tau_{\circ}$ = 1.5x10^{-8} s .

[1] (a) D. M. L. Goodgame, M. Goodgame, F. A. Cotton, *Inorg. Chem.* **1962**, *1*, 239-245; (b) F. A. Cotton, D. M. Goodgame, O. D. Faut, R. H. Holm, *J. Am. Chem. Soc.* **1961**, *83*, 1780-&; (c) A. Mirceva, *Vestn. Slov. Kem. Drus.* **1987**, *34*, 449; (d) D. M. L. Goodgame, M. Goodgame, *Inorg. Chem.* **1965**, *4*, 139-143.

[2] G. M. Sheldrick., in *SADABS: A program for absorption correction with the Bruker SMART system*, University of Göttingen, Germany, **2008**.

[3] G. M. Sheldrick, in *SHELXS-97, Program for Crystal Structure Determination*, University of Göttingen, Göttingen, Germany, **1997**.

[4] G. M. Sheldrick, *Acta Crystallogr. Sec. A* **2008**, *64*, 112-122.