Rare single-molecule magnets with six-coordinate Ln^{III} ion exhibiting trigonal antiprism configuration

Min-Xia Yao,* Zhao-Xia Zhu, Xing-Yun Lu, Xiao-Wei Deng, and Su Jing*

School of Chemistry and Molecular Engineering, Nanjing Tech University, Nanjing, 211816, P. R. China.

Supporting information

Table S1 Summary of crystallographic data for the complexes **1**–**4**.

	1	**2**	**3**	**4**
formula	$C_{60}H_{68}GdN_9Ni_2O_{16}$	$C_{60}H_{68}N_9Ni_2O_{16}Tb$	$C_{60}H_{68}DyN_9Ni_2O_{16}$	$C_{65}H_{79.30}ClDyN_8Ni_2O_{17.65}$
fw	1445.90	1447.57	1451.15	1570.43
crystal system	Triclinic	Triclinic	Triclinic	Triclinic
space group	P_{-1}	P_{-1}	P_{-1}	P_{-1}
a, Å	13.2375(6)	13.2669(7)	13.3101(7)	13.256(6)
b, Å	15.1226(9)	15.1167(7)	15.1304(8)	15.998(7)
c, Å	17.6501(10)	17.6076(10)	17.5472(7)	17.783(8)
a, deg	72.987(2)	73.3906(17)	73.642(2)	71.046(7)
β, deg	89.432(3)	89.3892(19)	89.254(3)	88.592(7)
γ, deg	66.867(2)	66.6355(16)	66.439(2)	68.988(6)
V, Å^3	3084.8(3)	3085.2(3)	3088.1(3)	3312(3)
Z	2	2	2	2
ρ_{calcd}, g cm^{-3}	1.557	1.558	1.561	1.575
T / K	173(2)	173(2)	173(2)	296(2)
μ, mm^{-1}	1.742	1.813	1.876	1.796
θ, deg	3.08 to 27.00	3.08 to 25.40	3.07 to 25.41	1.45 to 26.50
F(000)	1478	1480	1482	1611
index ranges	-16<=h<=16 -18<=k<=19 -20<=l<=22	-16<=h<=15 -18<=k<=17 -18<=l<=21	−15 ≤ h ≤ 16 −18 ≤ k ≤ 18 −20 ≤ l ≤ 21	-16<=h<=16 -20<=k<=20 -22<=l<=18
data/restraints /parameters	13213 / 2 / 811	11011 / 0 / 799	11057 / 0 / 805	13535 / 389 / 963

* To whom correspondence should be addressed. Email: yaomx@njtech.edu.cn. Fax: +86-25-58139528. Nanjing Tech University.

GOF (F^2)	1.073	1.064	1.040	1.014
$R_1{}^a$,$wR_2{}^b$	0.0409	0.0365	0.0346	0.0733
(I>2σ(I))	0.1129	0.1036	0.0879	0.1783
$R_1{}^a$, $wR_2{}^b$	0.0584	0.0543	0.0593	0.1330
(all data)	0.1170	0.1124	0.0946	0.2180

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

Table S2 Selected bond lengths (Å) and angles (°) for **1**.

N(10)-Ni(1)	2.105(3)	N(12)-Ni(1)	2.099(3)
N(13)-Ni(1)	2.125(3)	N(14)-Ni(2)	2.082(3)
N(16)-Ni(2)	2.111(3)	N(17)-Ni(2)	2.083(3)
Ni(1)-O(5)	2.064(2)	Ni(1)-O(2)	2.076(2)
Ni(1)-O(3)	2.079(2)	Ni(1)-Gd(1)	3.3211(5)
Ni(2)-O(11)	2.070(2)	Ni(2)-O(9)	2.075(2)
Ni(2)-O(8)	2.092(2)	Ni(2)-Gd(1)	3.3001(5)
O(2)-Gd(1)	2.419(2)	O(3)-Gd(1)	2.351(2)
O(4)-Gd(1)	2.904(2)	O(5)-Gd(1)	2.396(2)
O(8)-Gd(1)	2.389(2)	O(9)-Gd(1)	2.376(2)
O(11)-Gd(1)	2.342(2)	O(5)-Ni(1)-O(2)	77.16(9)
O(5)-Ni(1)-O(3)	76.06(9)	O(2)-Ni(1)-O(3)	76.47(10)
O(5)-Ni(1)-N(12)	164.32(11)	O(2)-Ni(1)-N(12)	98.04(10)
O(3)-Ni(1)-N(12)	88.33(11)	O(5)-Ni(1)-N(10)	98.74(10)
O(2)-Ni(1)-N(10)	88.58(10)	O(3)-Ni(1)-N(10)	164.89(11)
N(12)-Ni(1)-N(10)	96.02(11)	O(5)-Ni(1)-N(13)	87.44(10)
O(2)-Ni(1)-N(13)	164.51(10)	O(3)-Ni(1)-N(13)	98.46(11)
N(12)-Ni(1)-N(13)	96.41(11)	N(10)-Ni(1)-N(13)	95.42(11)
O(11)-Ni(2)-O(9)	76.74(9)	O(11)-Ni(2)-N(14)	164.48(11)
O(9)-Ni(2)-N(14)	97.93(10)	O(11)-Ni(2)-N(17)	87.78(10)
O(9)-Ni(2)-N(17)	164.43(11)	N(14)-Ni(2)-N(17)	96.61(11)
O(11)-Ni(2)-O(8)	76.20(9)	O(9)-Ni(2)-O(8)	76.39(10)
N(14)-Ni(2)-O(8)	88.41(11)	N(17)-Ni(2)-O(8)	98.51(11)
O(11)-Ni(2)-N(16)	98.82(11)	O(9)-Ni(2)-N(16)	88.48(11)
N(14)-Ni(2)-N(16)	95.56(12)	N(17)-Ni(2)-N(16)	95.64(12)
O(8)-Ni(2)-N(16)	164.76(11)	O(11)-Gd(1)-O(3)	121.92(8)
O(11)-Gd(1)-O(9)	66.08(8)	O(3)-Gd(1)-O(9)	112.76(8)
O(11)-Gd(1)-O(8)	65.74(8)	O(3)-Gd(1)-O(8)	171.38(8)
O(9)-Gd(1)-O(8)	65.48(8)	O(11)-Gd(1)-O(5)	111.59(8)
O(3)-Gd(1)-O(5)	65.06(8)	O(9)-Gd(1)-O(5)	175.73(8)

O(8)-Gd(1)-O(5)	117.26(8)	O(11)-Gd(1)-O(2)	170.75(8)
O(3)-Gd(1)-O(2)	65.22(8)	O(9)-Gd(1)-O(2)	118.03(8)
O(8)-Gd(1)-O(2)	107.64(8)	O(5)-Gd(1)-O(2)	64.85(8)
O(11)-Gd(1)-O(4)	73.23(7)	O(3)-Gd(1)-O(4)	56.70(8)
O(9)-Gd(1)-O(4)	67.69(8)	O(8)-Gd(1)-O(4)	126.74(8)
O(5)-Gd(1)-O(4)	108.38(8)	O(2)-Gd(1)-O(4)	115.85(8)
O(11)-Gd(1)-O(12)	55.94(7)	O(3)-Gd(1)-O(12)	72.68(7)
O(9)-Gd(1)-O(12)	108.10(8)	O(8)-Gd(1)-O(12)	115.94(8)
O(5)-Gd(1)-O(12)	67.89(8)	O(2)-Gd(1)-O(12)	126.19(7)
O(4)-Gd(1)-O(12)	58.30(7)		

Table S3 Selected bond lengths (Å) and angles (°) for **2**.

N(10)-Ni(1)	2.098(3)	N(12)-Ni(1)	2.101(3)
N(13)-Ni(1)	2.109(3)	N(14)-Ni(2)	2.091(3)
N(16)-Ni(2)	2.095(3)	N(17)-Ni(2)	2.084(3)
Ni(1)-O(3)	2.063(3)	Ni(1)-O(5)	2.064(3)
Ni(1)-O(2)	2.073(3)	Ni(1)-Tb(1)	3.3153(5)
Ni(2)-O(11)	2.064(3)	Ni(2)-O(9)	2.072(3)
Ni(2)-O(8)	2.077(3)	Ni(2)-Tb(1)	3.3006(5)
O(2)-Tb(1)	2.402(3)	O(3)-Tb(1)	2.360(3)
O(5)-Tb(1)	2.398(3)	O(8)-Tb(1)	2.397(3)
O(9)-Tb(1)	2.386(3)	O(11)-Tb(1)	2.351(3)
O(3)-Ni(1)-O(5)	76.63(10)	O(3)-Ni(1)-O(2)	76.13(10)
O(5)-Ni(1)-O(2)	77.16(11)	O(3)-Ni(1)-N(10)	164.18(12)
O(5)-Ni(1)-N(10)	97.87(12)	O(2)-Ni(1)-N(10)	88.22(12)
O(3)-Ni(1)-N(12)	87.37(11)	O(5)-Ni(1)-N(12)	163.94(11)
O(2)-Ni(1)-N(12)	97.89(12)	N(10)-Ni(1)-N(12)	97.22(13)
O(3)-Ni(1)-N(13)	98.92(12)	O(5)-Ni(1)-N(13)	87.40(12)
O(2)-Ni(1)-N(13)	164.47(12)	N(10)-Ni(1)-N(13)	95.60(13)
N(12)-Ni(1)-N(13)	96.56(13)	O(11)-Ni(2)-O(9)	77.16(11)
O(11)-Ni(2)-O(8)	76.39(10)	O(9)-Ni(2)-O(8)	76.78(10)
O(11)-Ni(2)-N(17)	87.13(12)	O(9)-Ni(2)-N(17)	164.17(12)
O(8)-Ni(2)-N(17)	97.84(12)	O(11)-Ni(2)-N(14)	164.31(12)
O(9)-Ni(2)-N(14)	97.60(12)	O(8)-Ni(2)-N(14)	88.05(11)
N(17)-Ni(2)-N(14)	97.06(13)	O(11)-Ni(2)-N(16)	98.39(12)
O(9)-Ni(2)-N(16)	87.91(12)	O(8)-Ni(2)-N(16)	164.55(12)

N(17)-Ni(2)-N(16)	96.39(13)	N(14)-Ni(2)-N(16)	96.16(12)
O(11)-Tb(1)-O(3)	122.06(9)	O(11)-Tb(1)-O(9)	65.98(9)
O(3)-Tb(1)-O(9)	112.64(9)	O(11)-Tb(1)-O(8)	65.27(9)
O(3)-Tb(1)-O(8)	171.51(9)	O(9)-Tb(1)-O(8)	65.19(9)
O(11)-Tb(1)-O(5)	111.40(9)	O(3)-Tb(1)-O(5)	65.06(9)
O(9)-Tb(1)-O(5)	175.34(9)	O(8)-Tb(1)-O(5)	117.71(9)
O(11)-Tb(1)-O(2)	171.05(9)	O(3)-Tb(1)-O(2)	64.75(9)
O(9)-Tb(1)-O(2)	118.16(9)	O(8)-Tb(1)-O(2)	108.47(9)
O(5)-Tb(1)-O(2)	65.02(9)		

Table S4 Selected bond lengths (Å) and angles (°) for **3**.

Dy(1)-O(3)	2.329(2)	Dy(1)-O(11)	2.337(3)
Dy(1)-O(5)	2.371(3)	Dy(1)-O(2)	2.377(3)
Dy(1)-O(9)	2.377(3)	Dy(1)-O(8)	2.386(3)
Dy(1)-Ni(1)	3.2725(5)	Dy(1)-Ni(2)	3.2883(5)
N(1)-Ni(1)	2.078(4)	N(3)-Ni(1)	2.087(3)
N(4)-Ni(1)	2.103(4)	N(5)-Ni(2)	2.094(3)
N(7)-Ni(2)	2.118(3)	N(8)-Ni(2)	2.093(3)
Ni(1)-O(3)	2.069(3)	Ni(1)-O(5)	2.071(3)
Ni(1)-O(2)	2.086(3)	Ni(2)-O(9)	2.066(3)
Ni(2)-O(11)	2.070(3)	Ni(2)-O(8)	2.080(3)
O(3)-Dy(1)-O(11)	121.85(9)	O(3)-Dy(1)-O(5)	66.62(9)
O(11)-Dy(1)-O(5)	112.08(10)	O(3)-Dy(1)-O(2)	66.27(9)
O(11)-Dy(1)-O(2)	170.93(9)	O(5)-Dy(1)-O(2)	66.16(9)
O(3)-Dy(1)-O(9)	110.64(9)	O(11)-Dy(1)-O(9)	65.81(9)
O(5)-Dy(1)-O(9)	175.38(10)	O(2)-Dy(1)-O(9)	116.61(10)
O(3)-Dy(1)-O(8)	170.19(10)	O(11)-Dy(1)-O(8)	65.88(9)
O(5)-Dy(1)-O(8)	117.60(9)	O(2)-Dy(1)-O(8)	106.57(9)
O(9)-Dy(1)-O(8)	65.74(9)	O(3)-Ni(1)-O(5)	77.13(11)
O(3)-Ni(1)-N(1)	164.67(12)	O(5)-Ni(1)-N(1)	98.07(12)
O(3)-Ni(1)-N(3)	87.25(12)	O(5)-Ni(1)-N(3)	164.31(12)
N(1)-Ni(1)-N(3)	96.67(13)	O(3)-Ni(1)-O(2)	76.51(10)
O(5)-Ni(1)-O(2)	77.12(11)	N(1)-Ni(1)-O(2)	88.25(12)
N(3)-Ni(1)-O(2)	98.03(13)	O(3)-Ni(1)-N(4)	98.51(12)
O(5)-Ni(1)-N(4)	87.62(13)	N(1)-Ni(1)-N(4)	95.80(14)
N(3)-Ni(1)-N(4)	96.22(14)	O(2)-Ni(1)-N(4)	164.63(13)
O(9)-Ni(2)-O(11)	76.54(11)	O(9)-Ni(2)-O(8)	77.15(10)
O(11)-Ni(2)-O(8)	76.47(11)	O(9)-Ni(2)-N(8)	164.05(12)

O(11)-Ni(2)-N(8)	87.58(12)	O(8)-Ni(2)-N(8)	97.93(12)
O(9)-Ni(2)-N(5)	98.21(12)	O(11)-Ni(2)-N(5)	164.47(12)
O(8)-Ni(2)-N(5)	88.14(12)	N(8)-Ni(2)-N(5)	96.76(13)
O(9)-Ni(2)-N(7)	87.57(12)	O(11)-Ni(2)-N(7)	98.75(12)
O(8)-Ni(2)-N(7)	164.65(12)	N(8)-Ni(2)-N(7)	96.41(13)
N(5)-Ni(2)-N(7)	95.58(13)		

Table S5 Selected bond lengths (Å) and angles (°) for **4**.

Dy(1)-O(9)	2.333(5)	Dy(1)-O(8)	2.359(5)
Dy(1)-O(3)	2.361(5)	Dy(1)-O(5)	2.363(5)
Dy(1)-O(2)	2.365(5)	Dy(1)-O(11)	2.392(5)
Ni(1)-O(3)	2.054(5)	Ni(1)-O(5)	2.061(5)
Ni(1)-N(3)	2.095(7)	Ni(1)-O(2)	2.095(5)
Ni(1)-N(1)	2.108(7)	Ni(1)-N(4)	2.119(7)
Ni(2)-O(11)	2.059(6)	Ni(2)-O(9)	2.077(5)
Ni(2)-N(7)	2.091(6)	Ni(2)-O(8)	2.094(5)
Ni(2)-N(8)	2.103(7)	Ni(2)-N(5)	2.106(7)
O(9)-Dy(1)-O(8)	67.69(18)	O(9)-Dy(1)-O(3)	106.33(18)
O(8)-Dy(1)-O(3)	167.15(19)	O(9)-Dy(1)-O(5)	170.54(19)
O(8)-Dy(1)-O(5)	121.37(18)	O(3)-Dy(1)-O(5)	65.37(18)
O(9)-Dy(1)-O(2)	115.14(19)	O(8)-Dy(1)-O(2)	104.88(19)
O(3)-Dy(1)-O(2)	66.62(18)	O(5)-Dy(1)-O(2)	66.74(19)
O(9)-Dy(1)-O(11)	66.08(19)	O(8)-Dy(1)-O(11)	66.14(19)
O(3)-Dy(1)-O(11)	122.92(19)	O(5)-Dy(1)-O(11)	113.80(18)
O(2)-Dy(1)-O(11)	170.20(17)	O(3)-Ni(1)-O(5)	76.6(2)
O(3)-Ni(1)-N(3)	88.0(2)	O(5)-Ni(1)-N(3)	164.5(2)
O(3)-Ni(1)-O(2)	77.4(2)	O(5)-Ni(1)-O(2)	77.5(2)
N(3)-Ni(1)-O(2)	97.3(2)	O(3)-Ni(1)-N(1)	164.1(2)
O(5)-Ni(1)-N(1)	96.1(2)	N(3)-Ni(1)-N(1)	98.3(3)
O(2)-Ni(1)-N(1)	87.2(2)	O(3)-Ni(1)-N(4)	96.1(2)

O(5)-Ni(1)-N(4)	87.9(2)	N(3)-Ni(1)-N(4)	96.0(3)
O(2)-Ni(1)-N(4)	165.0(2)	N(1)-Ni(1)-N(4)	97.7(3)
O(11)-Ni(2)-O(9)	77.1(2)	O(11)-Ni(2)-N(7)	96.3(2)
O(9)-Ni(2)-N(7)	87.8(2)	O(11)-Ni(2)-O(8)	77.2(2)
O(9)-Ni(2)-O(8)	77.6(2)	N(7)-Ni(2)-O(8)	165.0(2)
O(11)-Ni(2)-N(8)	88.5(3)	O(9)-Ni(2)-N(8)	165.4(3)
N(7)-Ni(2)-N(8)	96.3(3)	O(8)-Ni(2)-N(8)	97.1(2)
O(11)-Ni(2)-N(5)	164.5(2)	O(9)-Ni(2)-N(5)	97.0(3)
N(7)-Ni(2)-N(5)	97.8(3)	O(8)-Ni(2)-N(5)	87.6(3)
N(8)-Ni(2)-N(5)	96.4(3)		

Table S6. Results of the Continuous Shape Measure Analysisa geometry[a]

Geometry	CTPR-7	COC-7	PBPY-7
1	**5.95**	**8.66**	9.45

[a]CTPR-7 is the shape measure relative to the capped trigonal prism; COC-7 is the shape measure relative to the capped octahedron; PBPY-7 is the shape measure relative to the pentagonal bipyramid.

Geometry	OC-6	TPR-6	PPY-6
2	**8.32**	**11.40**	28.18
3	**7.87**	**11.04**	27.81
4	**8.10**	**9.97**	26.24

[a]OC-6 is the shape measure relative to the octahedron; TPR-6 is the shape measure relative to the trigonal prism; PPY-6 is the shape measure relative to the pentagonal pyramid. The number in bold corresponds to the closer ideal geometry to the real complexes.

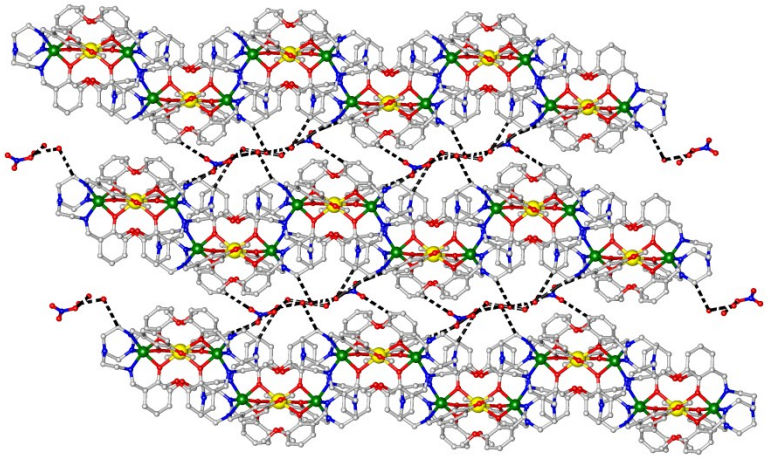

Figure S1. A view showing 3D structure formed by weak H-bonding interactions (black dash lines) in **1-3**.

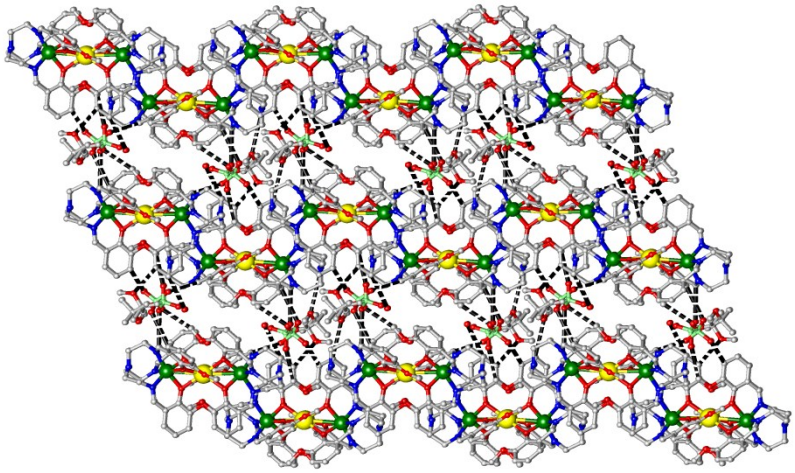

Figure S2. A view showing 3D structure formed by weak H-bonding interactions (black dash lines) in **4**.

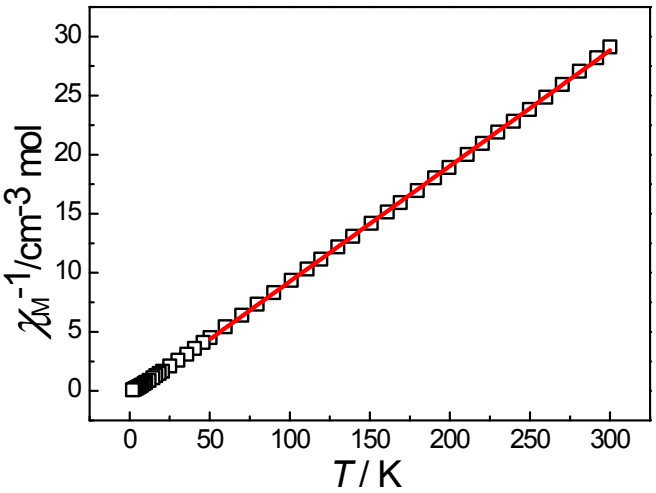

Figure S3. Plot of $1/\chi_M$ vs T for **1**. The red solid line represents the best fitting above 50 K gives the parameters C = 10.22 cm^3·K·mol^{-1}, θ = 5.42 K by Curie-Weiss law.

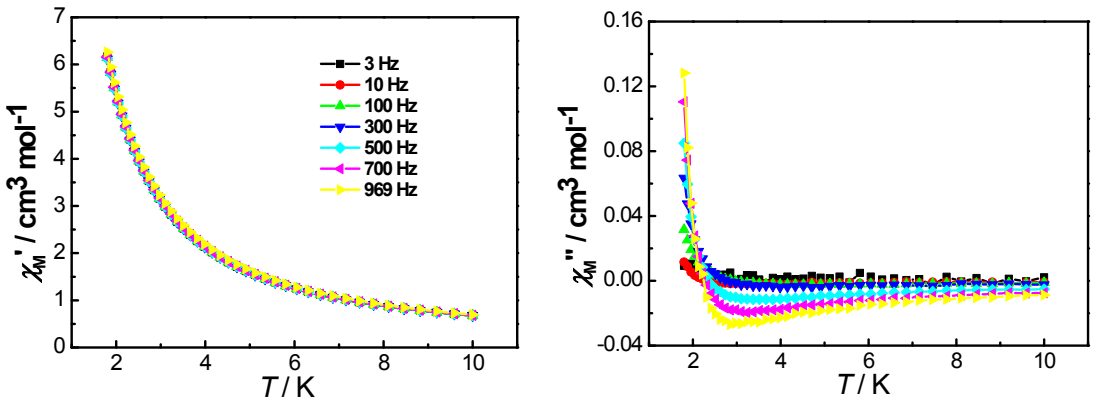

Figure S4. Temperature dependence of the in-phase χ' and out-of-phase χ'' in a 3 Oe ac field oscillating at 3- 969 Hz with a zero applied dc field for **2**.

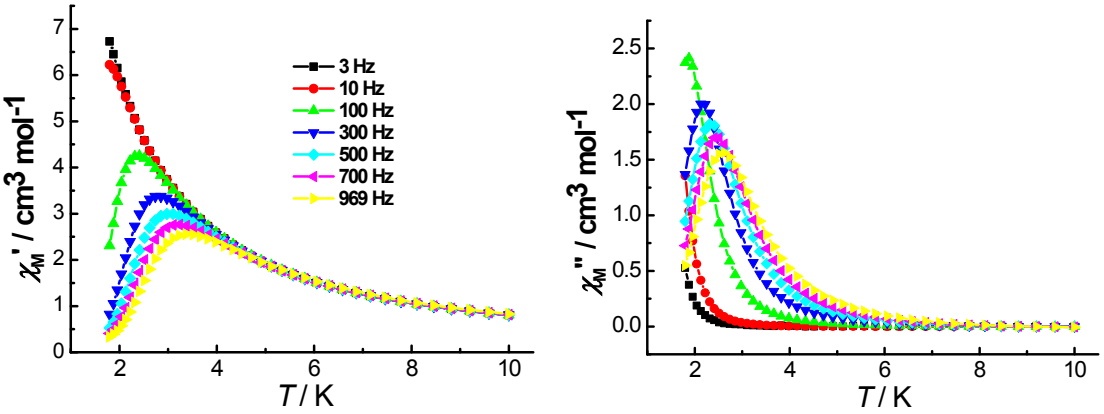

Figure S5. Temperature dependence of the in-phase χ' and out-of-phase χ'' in a 3 Oe ac field oscillating at 3- 969 Hz with a zero applied dc field for **3**.

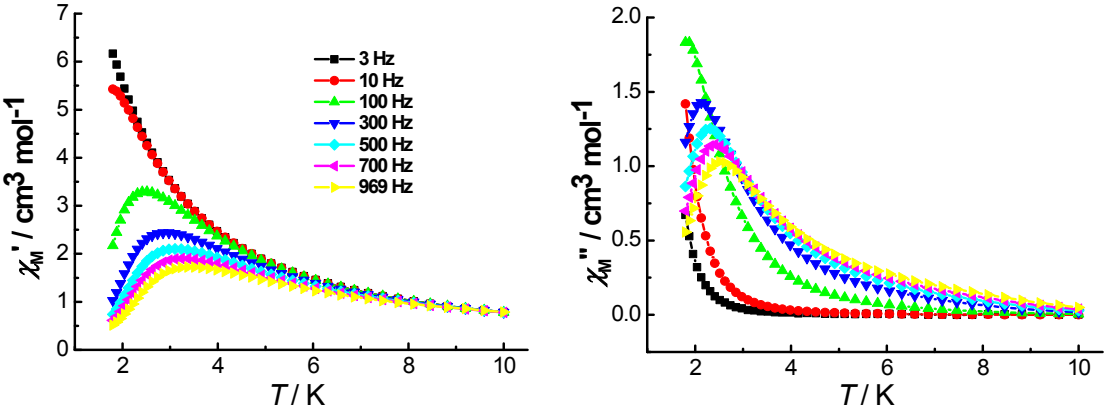

Figure S6. Temperature dependence of the in-phase χ' and out-of-phase χ'' in a 3 Oe ac field oscillating at 3- 969 Hz with a zero applied dc field for **4**.