New family of hetero-tri-metallic complexes [M(CuTb)]n (n = 1, 2, ∞; M=Co, Cr, Fe): synthesis, structure and tailored single-molecule magnet behavior

Nathalie Bridonneau*, Goeffrey Gontard, Valérie Marvaud*.

Supplementary Information

Trinuclear compounds

$[Co(CuTbL^1)].7H_2O$, noted (1)

$[Cr(CuTbL^1)].7H_2O$, noted (2)

$[Fe(CuTbL^1)].7H_2O$, noted (3)

Hexanuclear compounds

$[Co(CuTbL^2)]_2.14H_2O$, noted (4)

$[Cr(CuTbL^2)]_2.14H_2O$, noted (5)

$[Fe(CuTbL^2)]_2.14H_2O$, noted (6)

Pentagon chains

$\{Co(CuTbL^1)\}_n.7H_2O$, noted (7)

$\{Cr(CuTbL^1)\}_n.7H_2O$, noted (8)

$\{Fe(CuTbL^1)\}_n.7H_2O$, noted (9)

X-Ray Crystallography

Suitable crystals for X-ray crystallography were directly obtained from the reaction medium. A single crystal of the compounds was selected rapidly, mounted onto a glass fiber, and transferred in a cold nitrogen gas stream. Intensity data were collected with a Bruker-Nonius Kappa-CCD with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). Unit-cell parameters determination, data collection strategy and integration were carried out with the

Nonius EVAL-14 suite of programs. The structure was solved by direct methods using the SIR-92 program and refined anisotropically by full-matrix least-squares methods using the SHELXL-97 software package (G. M. Sheldrick, University of Göttingen, Germany, 1997).

Single Crystal X-Ray Structure of [Cr(CuTbL^1)].7H$_2$O (2)

The X-ray structure reveals that **2** is isostructural to the cobalt equivalent. The compound crystallizes in a monoclinic system with a P2$_1$/n space group. The cell parameters for **2** are *a* = 13.0818(3) Å, *b* = 12.1299(2) Å, *c* = 22.1408(5) Å, the cell volume is 3385.89(12) Å^3. The Cr-C distances range from 2.0509(0) to 2.0754(0) Å. The coordination spheres of the terbium and the copper are identical to the cobalt analogue.

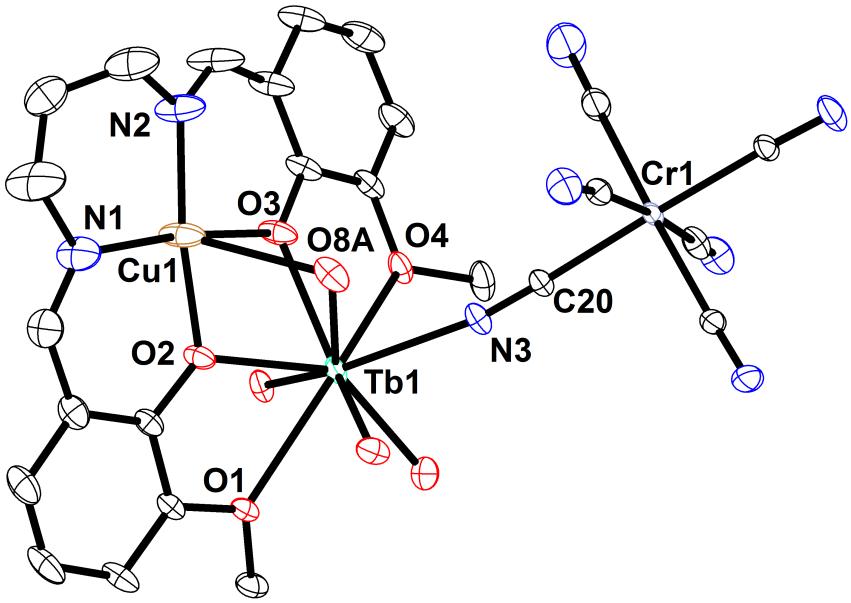

Figure S1. Ortep representation of the X-ray crystal structure of **2**
(thermal ellipsoids set at the 30 % probability level)

Single Crystal X-Ray Structure of [Fe(CuTbL^1)].7H$_2$O (3)

The X-ray structure reveals that **3** is isostructural to the cobalt equivalent. The compound crystallizes in a monoclinic system with a P2$_1$/n space group. The cell parameters for **3** are *a* = 12.8562(3) Å, *b* = 11.9304(3) Å, *c* = 22.1909(5) Å, the cell volume is 3279.95(14) Å^3. The Fe-C distances range from 1.9294(3) to 1.9399(38) Å. The coordination spheres of the terbium and the copper are identical to the cobalt analogue.

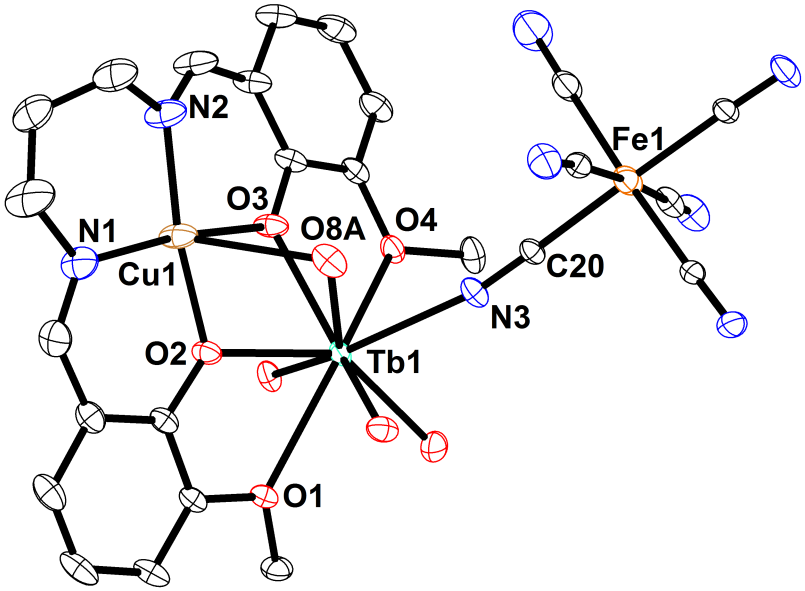

Figure S2. Ortep representation of the X-ray crystal structure of **3** (thermal ellipsoids set at the 30 % probability level)

Single Crystal X-Ray Structure of $[Cr(CuTbL^{2})]_2.14H_2O$ (5)

The X-ray structure reveals that **5** is isostructural to the cobalt equivalent **4**. The compound crystallizes in a monoclinic system with a $P2_1/c$ space group. The cell parameters for **5** are a = 26.0774(5) Å, b = 12.0578(2) Å, c = 22.9454(4) Å, the cell volume is 6837.17(21) $Å^3$. The Cr-C distances range from 2.0585(35) to 2.0856(37) Å. The coordination spheres of the terbium and the copper are identical to the cobalt analogue.

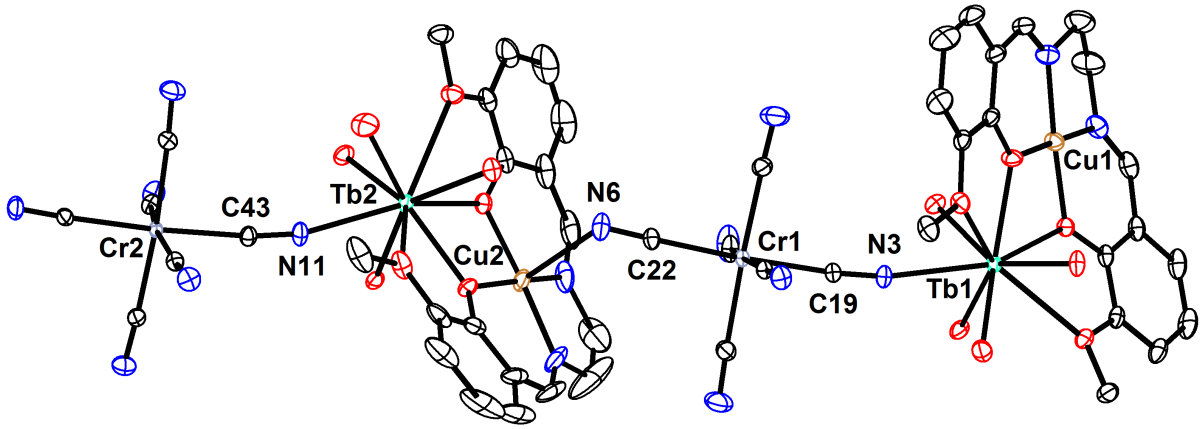

Figure S3. Ortep representation of the X-ray crystal structure of **5** (thermal ellipsoids set at the 30 % probability level)

Single Crystal X-Ray Structure of $[Fe(CuTbL^2)]_2.14H_2O$ (6)

The X-ray structure reveals that **6** is isostructural to the cobalt equivalent **4**. The compound crystallizes in a monoclinic system with a $P2_1/c$ space group. The cell parameters for **6** are *a* = 25.6467(6) Å, *b* = 11.9352(3) Å, *c* = 22.8151(6) Å, the cell volume is 6616.21(29) $Å^3$. The Fe-C distances range from 1.9264(30) to 1.9495(32) Å. The coordination spheres of the terbium and the copper are identical to the cobalt analogue.

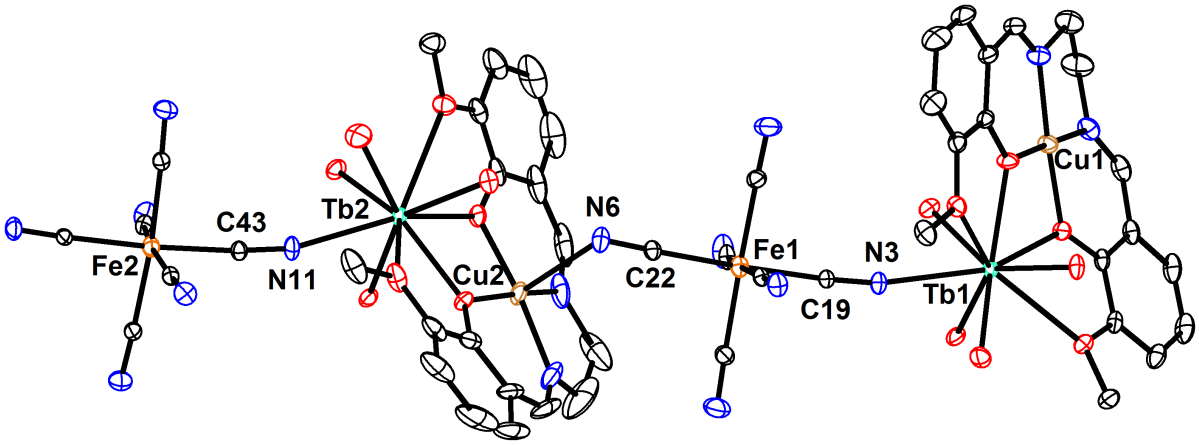

Figure S4. Ortep representation of the X-ray crystal structure of **6** (thermal ellipsoids set at the 30 % probability level)

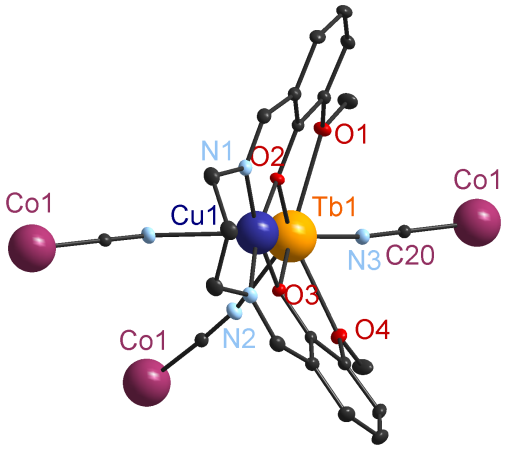

Figure S5. Representation of the X-ray crystal structure of **7** showing the ligand distorsion

Single Crystal X-Ray Structure of $[Cr(CuTbL^1)]_2.14H_2O$ (8)

The X-ray structure reveals that **8** is isostructural to the cobalt equivalent **7**. The compound crystallizes in a monoclinic system with a $P2_12_12_1$ space group. The cell parameters for **8** are a = 13.2421(3) Å, b = 15.1115(4) Å, c = 17.0360(4) Å, the cell volume 3409.04(14) $Å^3$. The coordination spheres of the terbium and the copper are identical to the cobalt analogue.

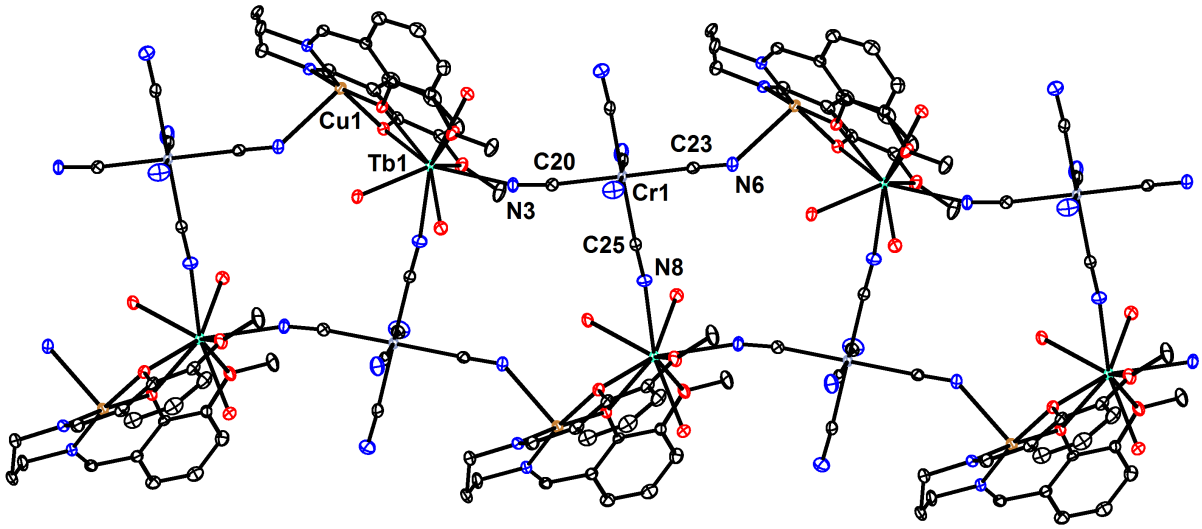

Figure S6. Ortep representation of the X-ray crystal structure of **8**

Crystal data and structure refinement for $[Co(CuTbL^1)].7H_2O$ (1)

Table 1. Crystal data and structure refinement for nb7-199, Compound **1**.

Identification code	nb7-199	
Empirical formula	C25 H34 Co Cu N8 O11 Tb	
Formula weight	903.99	
Temperature	200(1) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 12.7684(3) Å	α= 90°.
	b = 11.8653(3) Å	β= 105.329(2)°.
	c = 22.2188(5) Å	γ = 90°.
Volume	3246.41(14) $Å^3$	
Z	4	
Density (calculated)	1.850 g/cm^3	
Absorption coefficient	15.841 mm^{-1}	
F(000)	1796	
Crystal size	0.3 x 0.15 x 0.05 mm^3	
Theta range for data collection	4.126 to 66.521°.	
Index ranges	-15<=h<=15, -11<=k<=14, -25<=l<=26	
Reflections collected	19513	
Independent reflections	5670 [R(int) = 0.0429]	
Completeness to theta = 66.52°	99.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.2514 and 0.0760	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5670 / 0 / 435	
Goodness-of-fit on F^2	1.030	
Final R indices [I>2sigma(I)]	R1 = 0.0367, wR2 = 0.1006	
R indices (all data)	R1 = 0.0395, wR2 = 0.1043	
Largest diff. peak and hole	0.796 and -0.734 $e.Å^{-3}$	

Crystal data and structure refinement for $[Cr(CuTbL^1)].7H_2O$ (2)

Table 2. Crystal data and structure refinement for nb7-209, Compound **2**

Identification code	nb7-209	
Empirical formula	C25 H34 Cr Cu N8 O11 Tb	
Formula weight	897.06	
Temperature	200(1) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 13.0818(3) Å	α= 90°.
	b = 12.1299(2) Å	β= 105.4790(10)°.
	c = 22.1408(5) Å	γ = 90°.
Volume	3385.89(12) $Å^3$	
Z	4	
Density (calculated)	1.760 g/cm^3	
Absorption coefficient	3.070 mm^{-1}	
F(000)	1784	
Crystal size	0.3 x 0.1 x 0.05 mm^3	
Theta range for data collection	1.642 to 30.545°.	
Index ranges	-18<=h<=18, -17<=k<=17, -31<=l<=31	
Reflections collected	56207	
Independent reflections	10377 [R(int) = 0.0214]	
Completeness to theta = 30.55°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.564 and 0.441	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10377 / 0 / 435	
Goodness-of-fit on F^2	1.046	
Final R indices [I>2sigma(I)]	R1 = 0.0339, wR2 = 0.0865	
R indices (all data)	R1 = 0.0445, wR2 = 0. 0988	
Largest diff. peak and hole	1.873 and -2.816 e.$Å^{-3}$	

Crystal data and structure refinement for $[Fe(CuTbL^1)].7H_2O$ (3)

Table 3. Crystal data and structure refinement for nb8-44, compound **3**

Identification code	nb8-44	
Empirical formula	C25 H34 Cu Fe N8 O11 Tb	
Formula weight	900.91	
Temperature	200(1) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 12.8562(3) Å	α= 90°.
	b = 11.9304(3) Å	β= 105.493(2)°.
	c = 22.1909(5) Å	γ = 90°.
Volume	3279.95(14) $Å^3$	
Z	4	
Density (calculated)	1.824 g/cm^3	
Absorption coefficient	3.280 mm^{-1}	
F(000)	1792	
Crystal size	0.4 x 0.35 x 0.05 mm^3	
Theta range for data collection	1.665 to 30.587°.	
Index ranges	-18<=h<=18, -17<=k<=17, -31<=l<=31	
Reflections collected	56260	
Independent reflections	10028 [R(int) = 0.0225]	
Completeness to theta = 30.59°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.100 and 0.055	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10028 / 0 / 435	
Goodness-of-fit on F^2	1.069	
Final R indices [I>2sigma(I)]	R1 = 0.0273, wR2 = 0.0712	
R indices (all data)	R1 = 0.0337, wR2 = 0.0804	
Largest diff. peak and hole	1.395 and -1.638 $e.Å^{-3}$	

Crystal data and structure refinement for $[Co(CuTbL^2)]_2.14H_2O$ (4)

Table 4. Crystal data and structure refinement for nb8-39, compound **4**

Identification code	nb8-39	
Empirical formula	C48 H66 Co2 Cu2 N16 O23 Tb2	
Formula weight	1797.95	
Temperature	200(1) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 25.5005(6) Å	α= 90°.
	b = 11.9284(3) Å	β= 108.726(2)°.
	c = 22.7251(6) Å	γ = 90°.
Volume	6546.6(3) $Å^3$	
Z	4	
Density (calculated)	1.824 Mg/m^3	
Absorption coefficient	3.350 mm^{-1}	
F(000)	3568	
Crystal size	0.4 x 0.1 x 0.05 mm^3	
Theta range for data collection	2.092 to 30.600°.	
Index ranges	-36<=h<=36, -16<=k<=17, -32<=l<=32	
Reflections collected	195944	
Independent reflections	20102 [R(int) = 0.0265]	
Completeness to theta = 30.60°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7461 and 0.666	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	20102 / 0 / 842	
Goodness-of-fit on F^2	1.059	
Final R indices [I>2sigma(I)]	R1 = 0.0282, wR2 = 0.0623	
R indices (all data)	R1 = 0.0390, wR2 = 0.0702	
Largest diff. peak and hole	2.500 and -2.641 $e.Å^{-3}$	

Crystal data and structure refinement for $[Cr(CuTbL^2)]_2.14H_2O$ (5)

Table 5. Crystal data and structure refinement for Compound **5**

Identification code	nb8-95	
Empirical formula	C48 H66 Cr2 Cu2 N16 O23 Tb2	
Formula weight	1784.09	
Temperature	200(1) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 26.0774(5) Å	α= 90°
	b = 12.0578(2) Å	β= 108.621(2)°
	c = 22.9454(4) Å	γ = 90°
Volume	6837.2(2) $Å^3$	
Z	4	
Density (calculated)	1.733 $g.cm^{-3}$	
Absorption coefficient	3.041 mm^{-1}	
F(000)	3544	
Crystal size	0.4 x 0.1 x 0.05 mm^3	
θ range for data collection	2.062° to 30.643°	
Index ranges	-37<=h<=37, -17<=k<=17, -32<=l<=32	
Reflections collected	105964	
Independent reflections	20972 [R(int) = 0.0298]	
Completeness to θ = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.564 and 0.502	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	20972 / 12 / 842	
Goodness-of-fit on F^2	1.027	
Final R indices [I > 2σ(I)]	R1 = 0.0277, wR2 = 0.0613	
R indices (all data)	R1 = 0.0417, wR2 = 0.0679	
Largest difference peak and hole	1.490 and -1.816 $e.Å^{-3}$	

Crystal data and structure refinement for $[Fe(CuTbL^2)]_2.14H_2O$ (6)

Table 6. Crystal data and structure refinement for nb7-191, compound **6**.

Identification code	nb7-191	
Empirical formula	C48 H66 Cu2 Fe2 N16 O23 Tb2	
Formula weight	1791.78	
Temperature	200(1) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 25.6467(6) Å	α= 90°
	b = 11.9352(3) Å	β= 108.669(2)°
	c = 22.8151(6) Å	γ = 90°
Volume	6616.2(3) $Å^3$	
Z	4	
Density (calculated)	1.799 $g.cm^{-3}$	
Absorption coefficient	3.252 mm^{-1}	
F(000)	3560	
Crystal size	0.25 x 0.1 x 0.05 mm^3	
θ range for data collection	0.838° to 30.547°	
Index ranges	-36<=h<=36, -16<=k<=17, -32<=l<=32	
Reflections collected	202369	
Independent reflections	20233 [R(int) = 0.0293]	
Completeness to θ = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.564 and 0.498	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	20233 / 0 / 842	
Goodness-of-fit on F^2	1.078	
Final R indices [I > 2σ(I)]	R1 = 0.0289, wR2 = 0.0631	
R indices (all data)	R1 = 0.0418, wR2 = 0.0722	
Largest difference peak and hole	2.326 and -2.032 $e.Å^{-3}$	

Crystal data and structure refinement for $\{Co(CuTbL^1)\}_n.7H_2O$ (7)

Table 7. Crystal data and structure refinement for nb8-41, compound **7**

Identification code	nb8-41	
Empirical formula	C25 H34 Co Cu N8 O11 Tb	
Formula weight	903.99	
Temperature	200(1) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 12.9082(3) Å	α= 90°
	b = 14.9710(4) Å	β= 90°
	c = 16.9463(4) Å	γ = 90°
Volume	3274.85(14) $Å^3$	
Z	4	
Density (calculated)	1.834 $g.cm^{-3}$	
Absorption coefficient	3.348 mm^{-1}	
F(000)	1796	
Crystal size	0.4 x 0.1 x 0.05 mm^3	
θ range for data collection	2.404° to 30.571°	
Index ranges	-18<=h<=18, -21<=k<=21, -24<=l<=24	
Reflections collected	49038	
Independent reflections	10033 [R(int) = 0.0216]	
Completeness to θ = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.648 and 0.526	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10033 / 0 / 435	
Goodness-of-fit on F^2	1.053	
Final R indices [I > 2σ(I)]	R1 = 0.0146, wR2 = 0.0331	
R indices (all data)	R1 = 0.0166, wR2 = 0.0339	
Absolute structure parameter	-0.035(2)	
Largest difference peak and hole	0.651 and -0.326 $e.Å^{-3}$	

Crystal data and structure refinement for $\{Cr(CuTbL^{1})\}_{n}.7H_2O$ (8)

Table 8. Crystal data and structure refinement for nb7-209c, compound **8**

Identification code	nb7-209c	
Empirical formula	C25 H34 Cr Cu N8 O11 Tb	
Formula weight	897.06	
Temperature	200(1) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 13.2421(3) Å	α= 90°
	b = 15.1115(4) Å	β= 90°
	c = 17.0360(4) Å	γ = 90°
Volume	3409.04(14) $Å^3$	
Z	4	
Density (calculated)	1.748 $g.cm^{-3}$	
Absorption coefficient	3.049 mm^{-1}	
F(000)	1784	
Crystal size	0.4 x 0.02 x 0.02 mm^3	
θ range for data collection	2.369° to 30.559°	
Index ranges	-18<=h<=18, -21<=k<=21, -24<=l<=24	
Reflections collected	73633	
Independent reflections	10451 [R(int) = 0.0590]	
Completeness to θ = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.648 and 0.583	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10451 / 0 / 435	
Goodness-of-fit on F^2	1.011	
Final R indices [I > 2σ(I)]	R1 = 0.0267, wR2 = 0.0486	
R indices (all data)	R1 = 0.0353, wR2 = 0.0510	
Absolute structure parameter	-0.025(4)	
Largest difference peak and hole	0.818 and -0.411 $e.Å^{-3}$	

Magnetic Properties

Magnetic properties for [Co(CuTbL^1)].7H$_2$O (1)

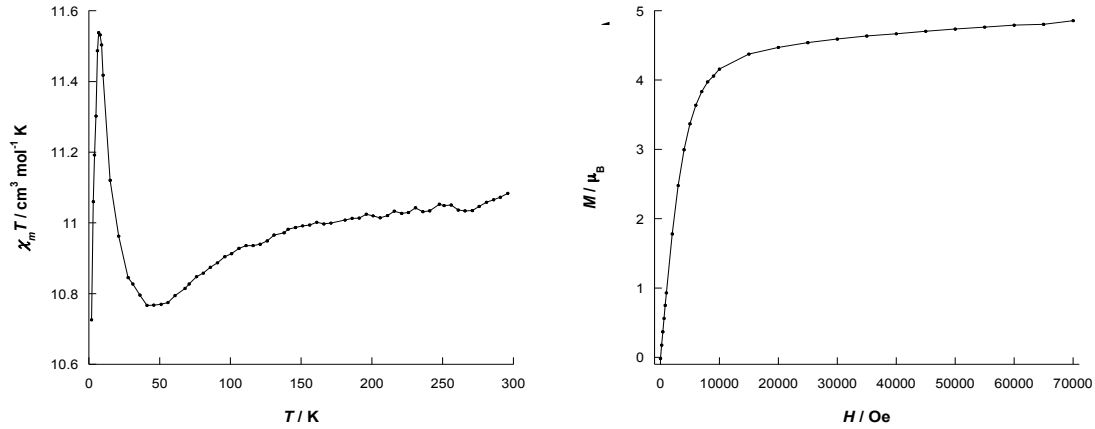

Figure S7: Variation of χT vs. T (H=1000G) and M vs. H at 2K for **1**

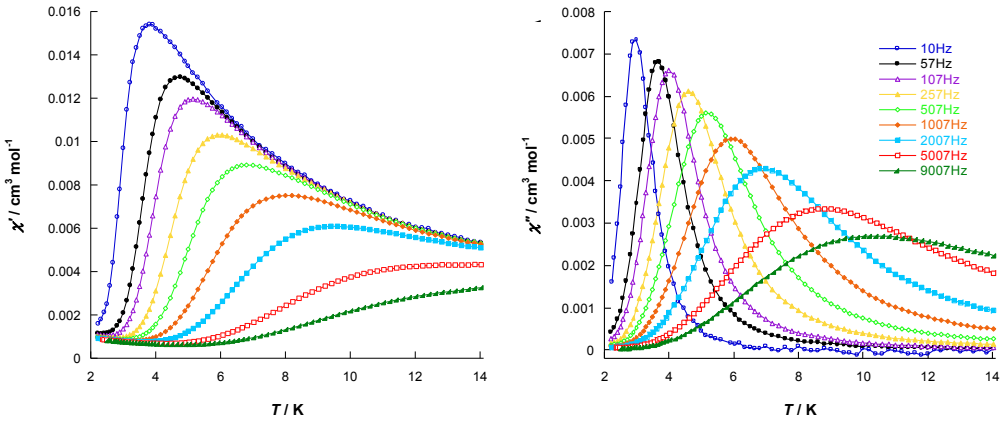

Figure *S8*: AC measurements at 1600 Oe (10Hz – 9007 Hz) for **1**

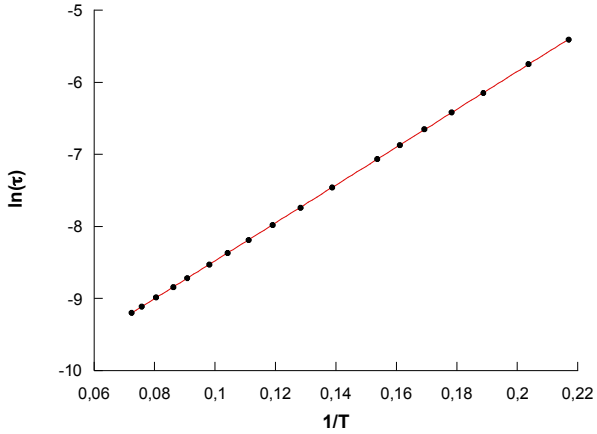

Figure *S9*: Arrhénius plot for **1**

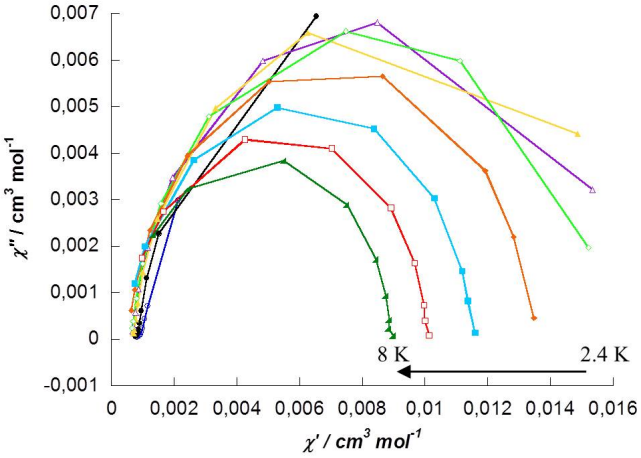

Figure *S10*: Cole-Cole plot for **1** in the temperature range 2.4 K – 8 K

Magnetic properties for [Cr(CuTbL^1)].7H$_2$O (2)

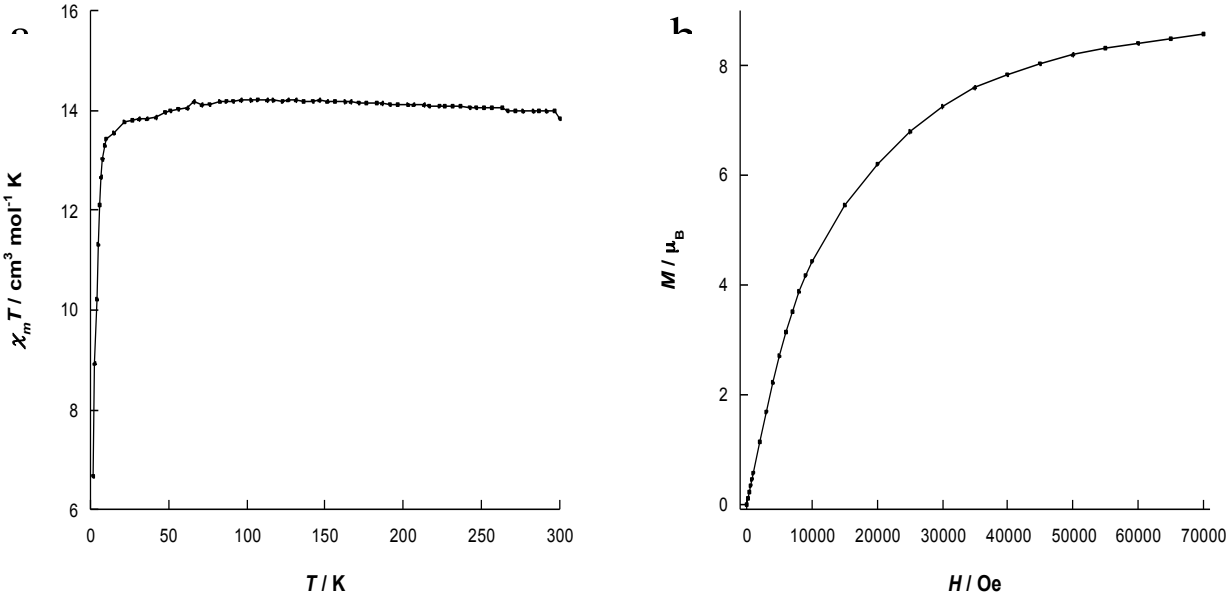

Figure *S11*: Variation of χT vs. T (H=1000G) and M vs. H at 2K for **2**

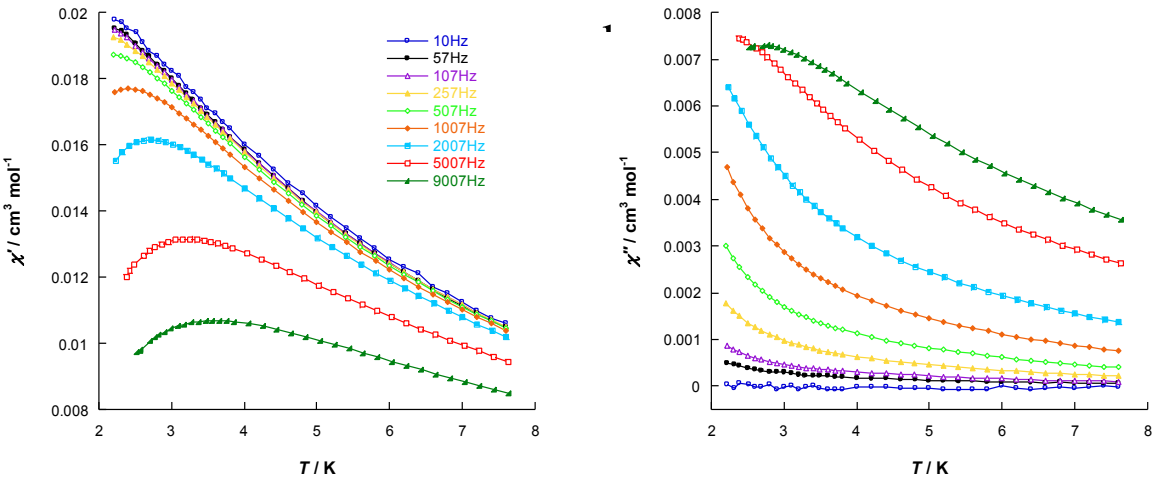

Figure *S12*: AC measurements at 1600 Oe (10Hz – 9007 Hz) for **2**

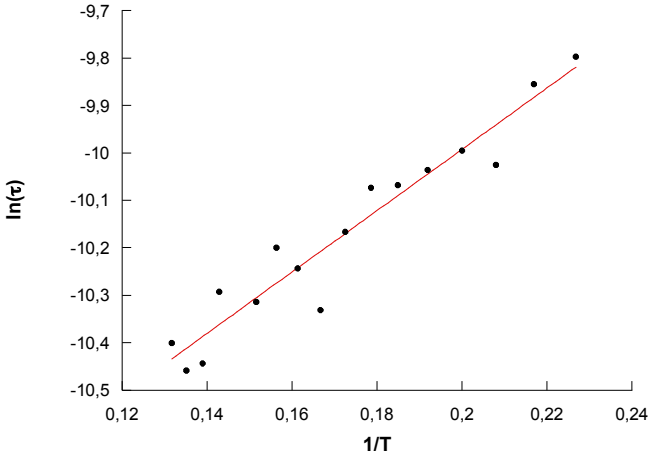

Figure *S13*: Arrhénius plot for **2**

Magnetic properties for [Fe(CuTbL^1)].7H$_2$O (3)

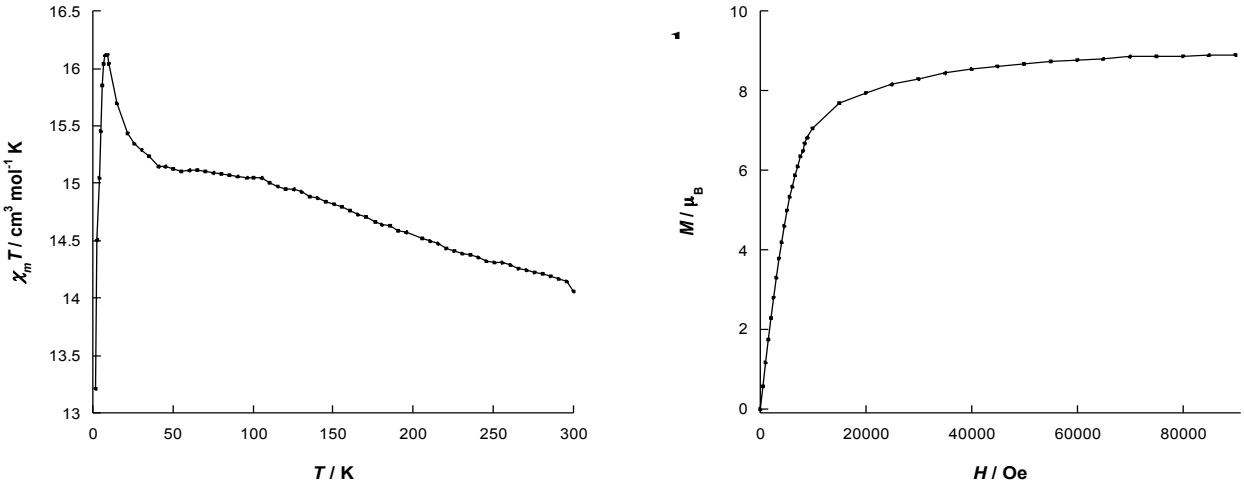

Figure *S14*: Variation of χT vs. T (H=1000G) and M vs. H at 2K for **3**

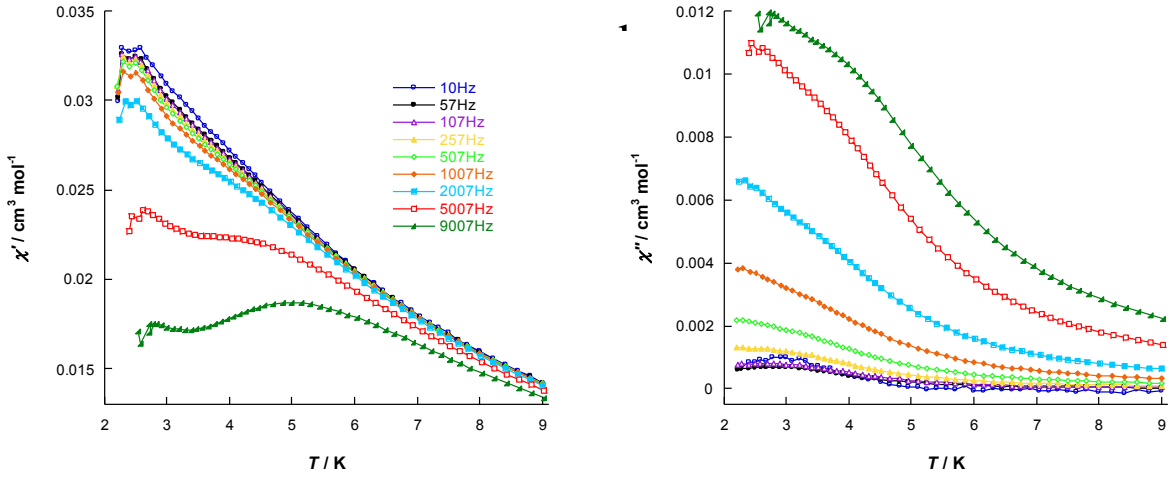

Figure *S15*: AC measurements at 1600 Oe (10Hz – 9007 Hz) for **3**

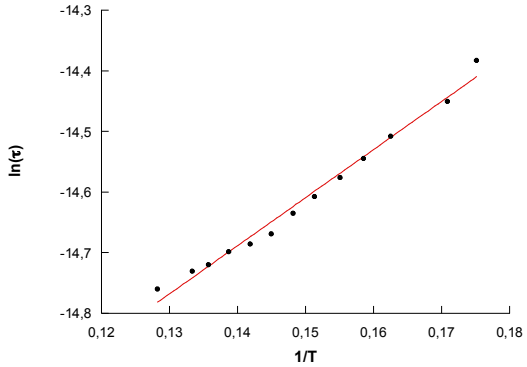

Figure *S16*: Arrhénius plot for **3**

Magnetic properties for $[Co(CuTbL^2)]_2.14H_2O$ (4)

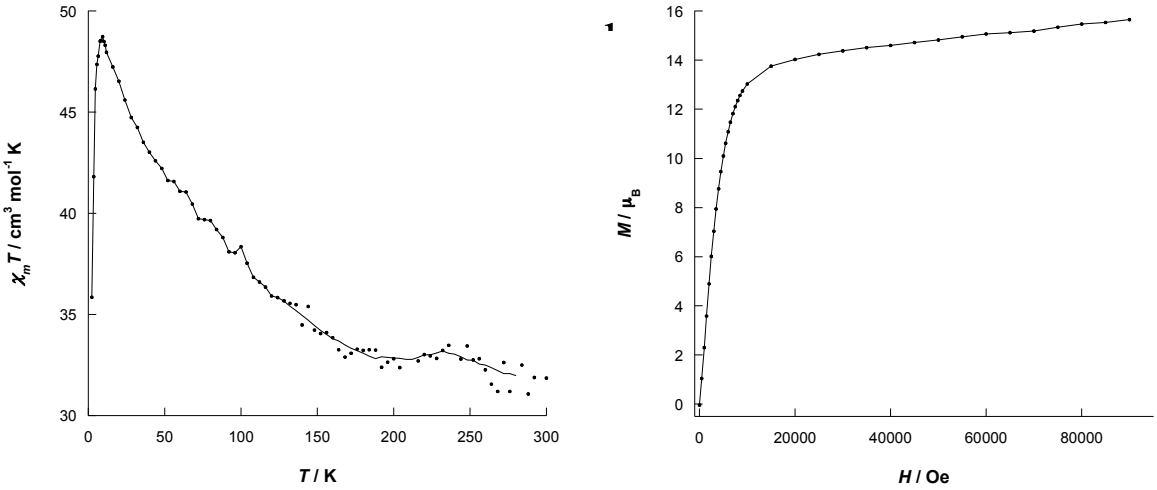

Figure *S17*: Variation of χT vs. T (H=1000G) and M vs. H at 2K for **4**

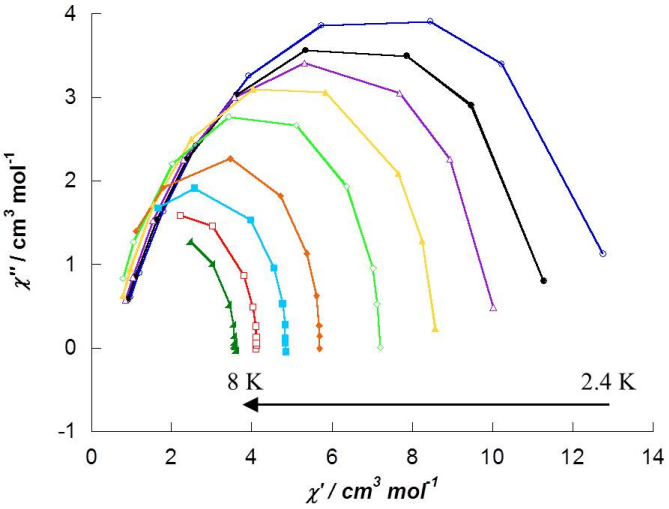

Figure *S18*: Cole-Cole plot for **4** in the temperature range 2.4 K – 8 K

Magnetic properties for $[Cr(CuTbL^2)]_2.14H_2O$ (5)

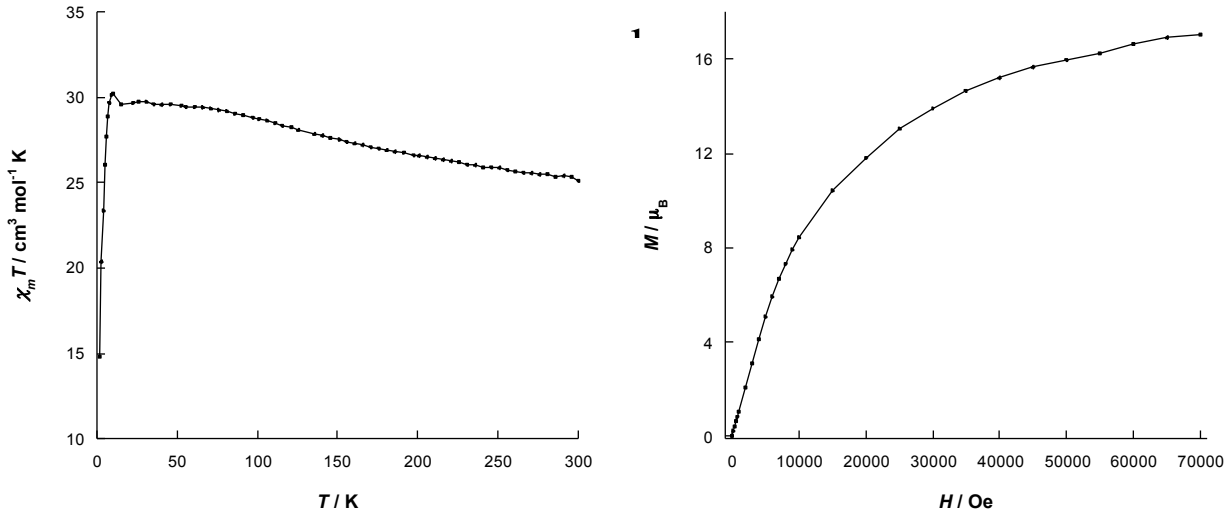

Figure *S19*: Variation of χT vs. T (H=1000G) and M vs. H at 2K for **5**

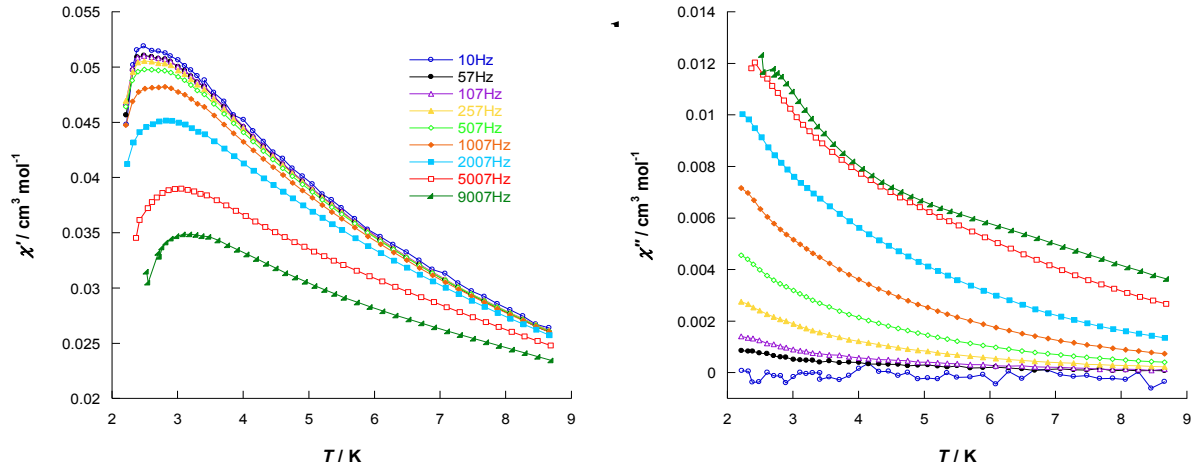

Figure *S20*: AC measurements at 1600 Oe (10Hz – 9007 Hz) for **5**

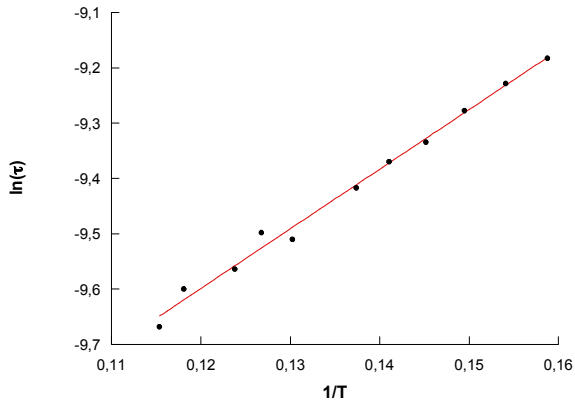

Figure *S21*: Arrhénius plot for **5**

Magnetic properties for $[Fe(CuTbL^2)]_2.14H_2O$ (6)

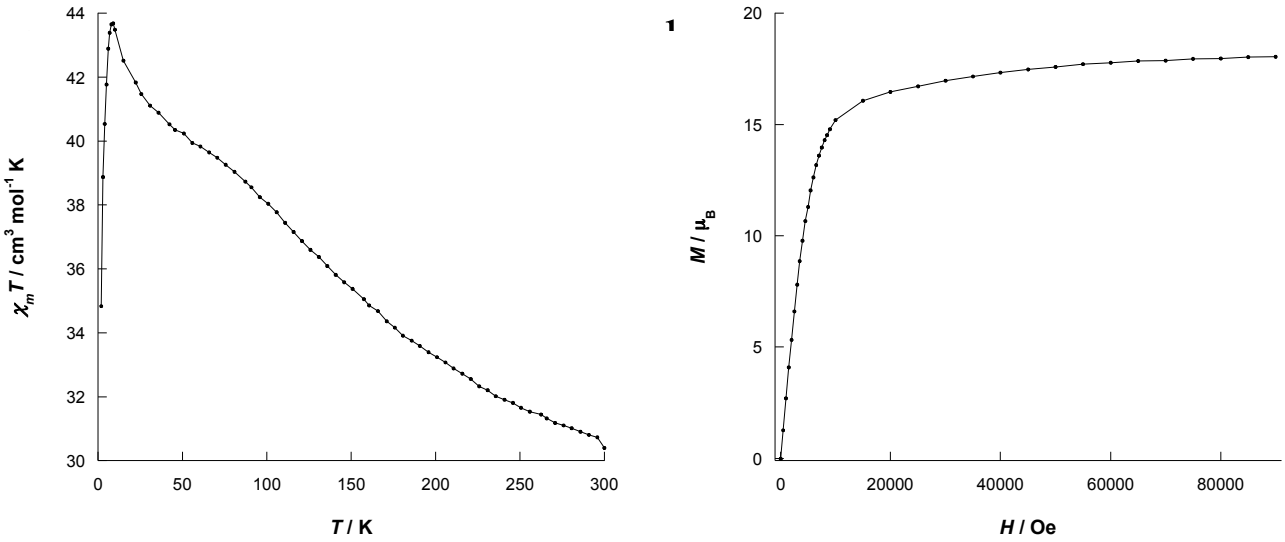

Figure *S22*: Variation of χT vs. T (H=1000G) and M vs. H at 2K for **6**

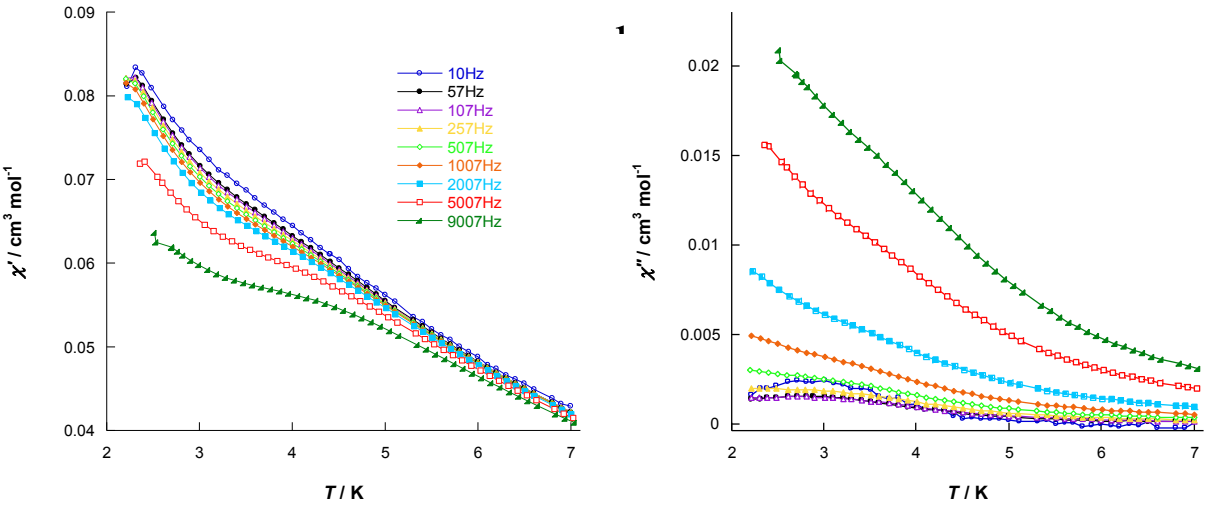

Figure *S23*: AC measurements at 1600 Oe (10Hz – 9007 Hz) for **6**

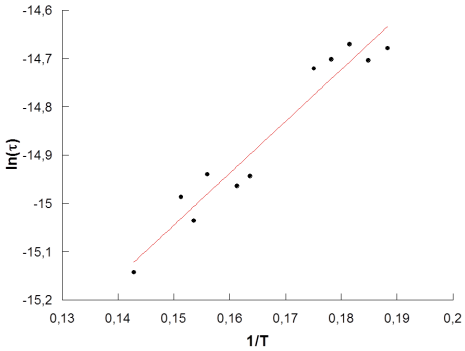

Figure *S24*: Arrhénius plot for **6**

Magnetic properties for $\{Co(CuTbL^1)\}_n.7H_2O$ (7)

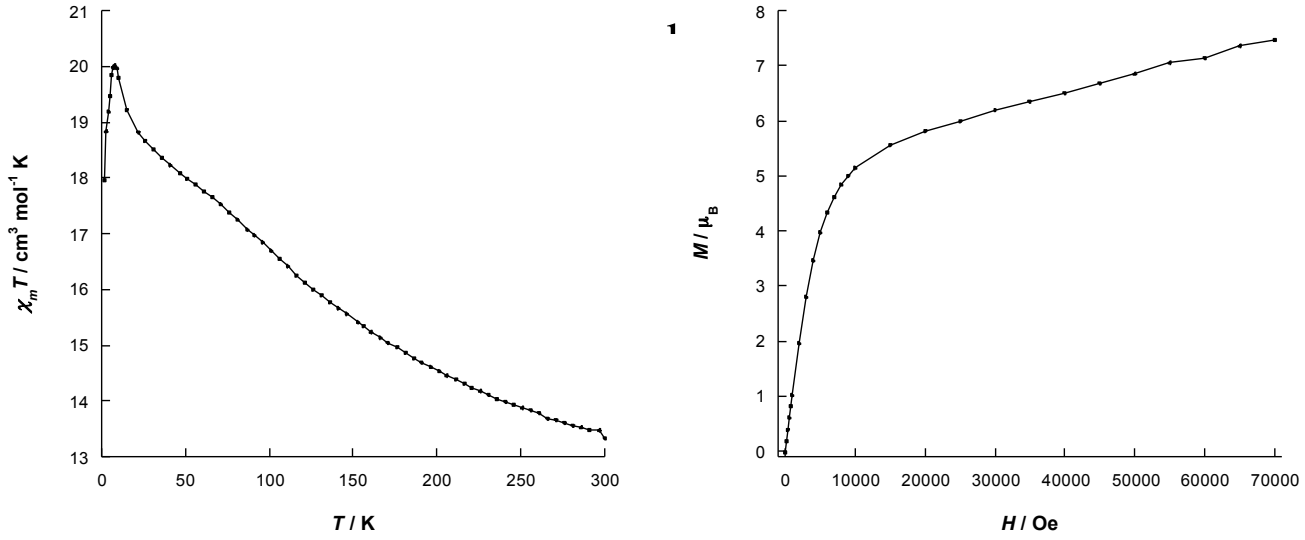

Figure *S25*: Variation of χT vs. T (H=1000G) and M vs. H at 2K for **7**

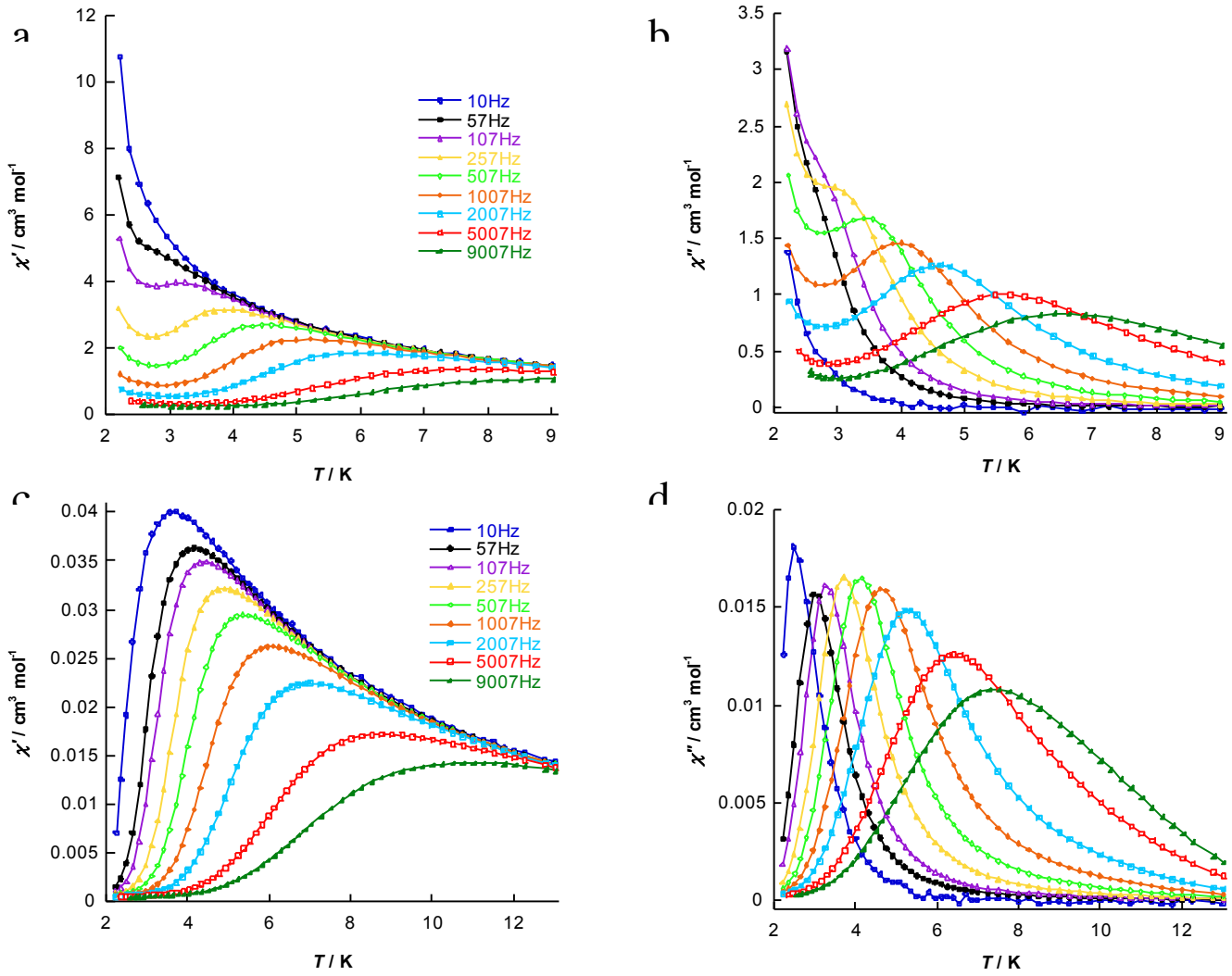

Figure *S25*: AC measurements at 0 Oe (10Hz – 9007 Hz) for **7** (a and b)

AC measurements at 1600 Oe (10Hz – 9007 Hz) for **7** (a and b)

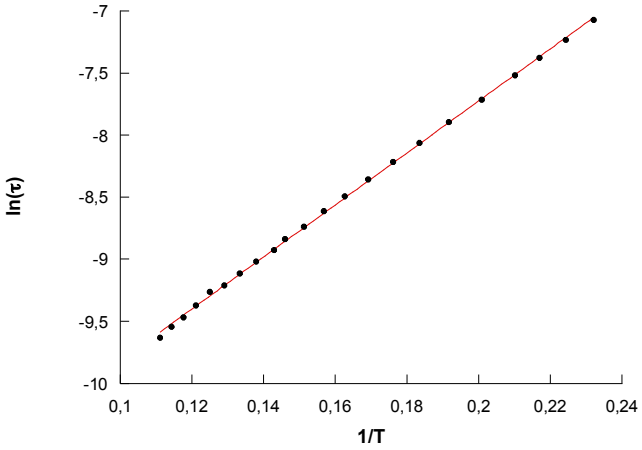

Figure *S27*: Arrhénius plot for **7**

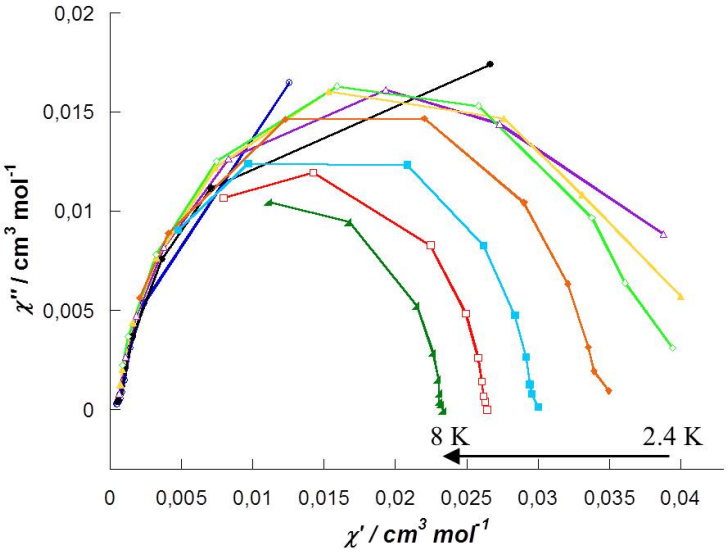

Figure *S28*: Cole-Cole plot for **7** in the temperature range 2.4 K – 8 K

Despite our efforts to avoid this effect, we observe for compounds **3**, **4**, **6**, and **7**, a continuous increase of chi*T by decreasing the temperature that is probably due to orientation of the crystals under the magnetic field in addition to spin orbit effect.

Magnetic properties for $\{Cr(CuTbL^1)\}_n.7H_2O$ (8)

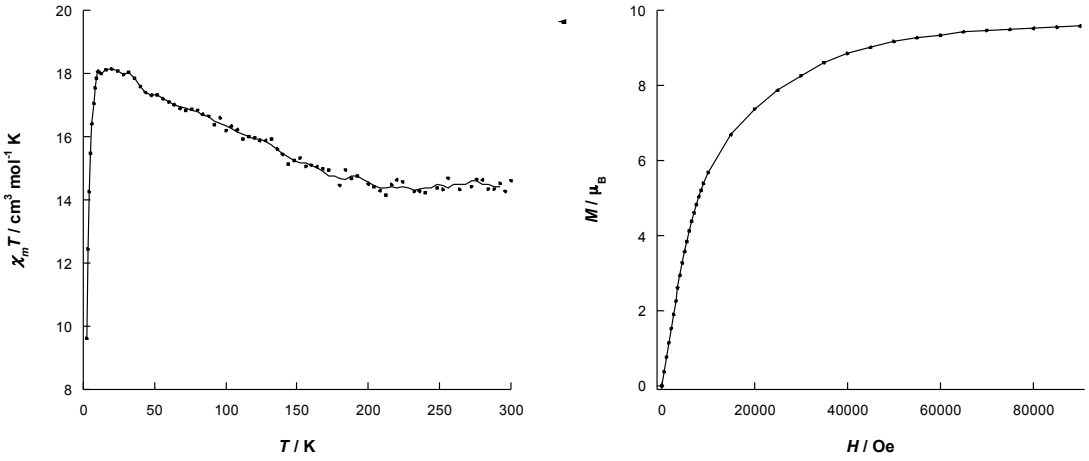

Figure *S29*: Variation of χT vs. T (H=1000G) and M vs. H at 2K for **8**

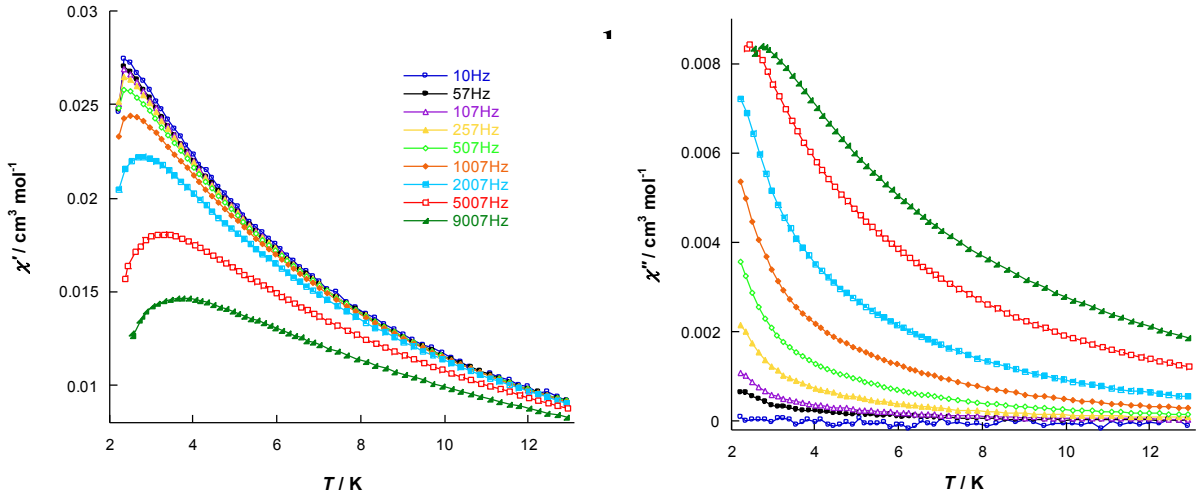

Figure *S30*: AC measurements at 1600 Oe (10Hz – 9007 Hz) for **8**

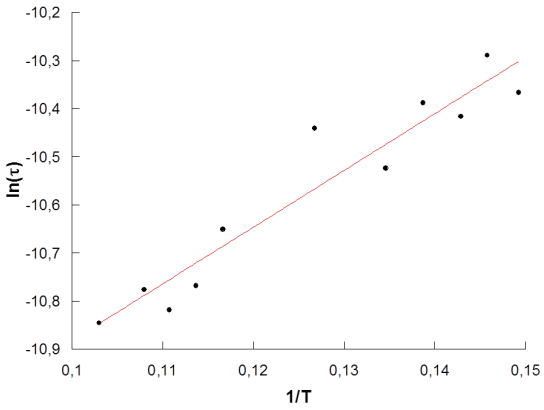

Figure *S31*: Arrhénius plot for **8**

Magnetic properties for $\{Fe(CuTbL^1)\}_n.7H_2O$ (9)

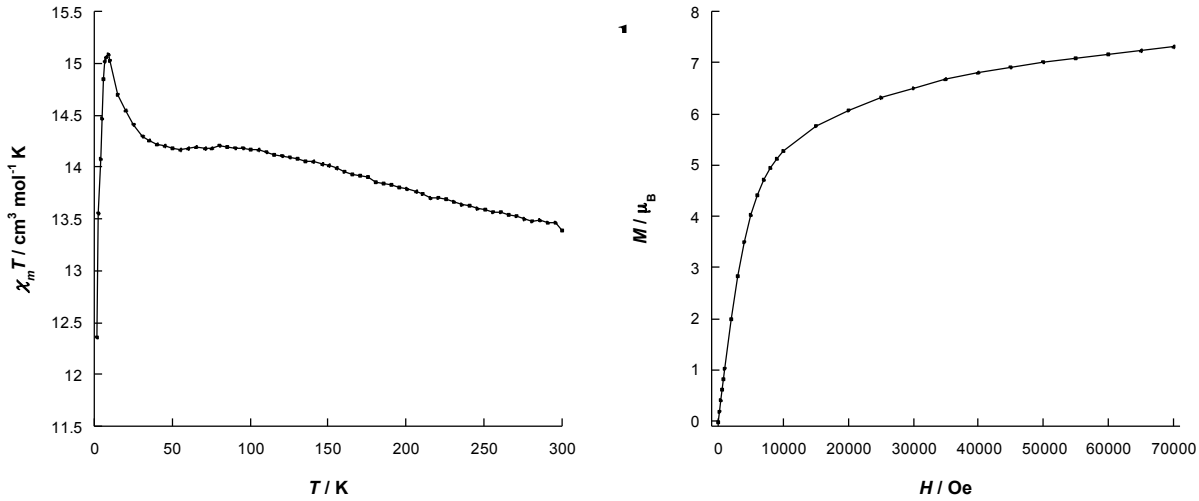

Figure *S32*: Variation of χT vs. T (H=1000G) and M vs. H at 2K for **9**

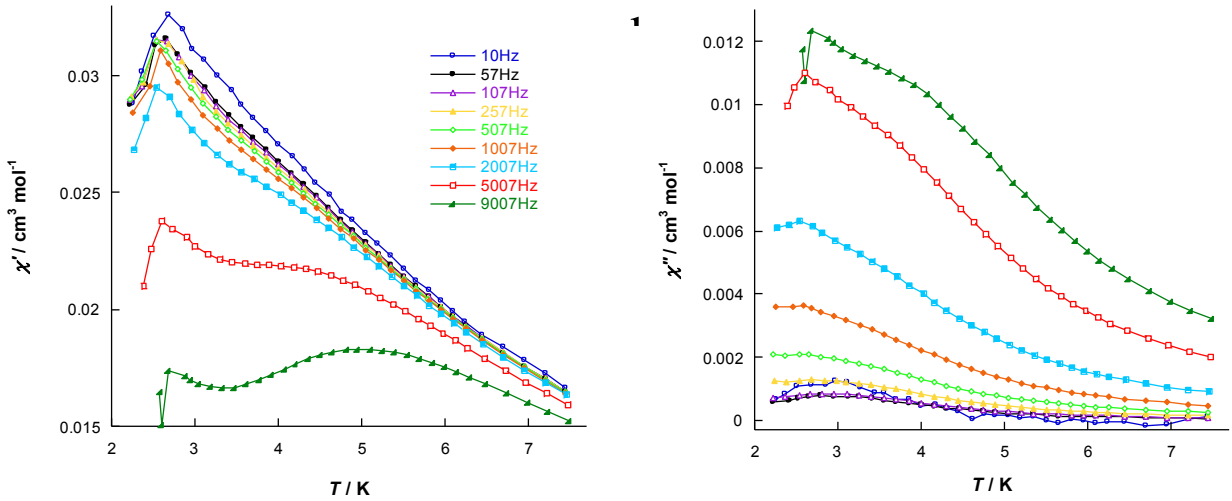

Figure *S33*: AC measurements at 1600 Oe (10Hz – 9007 Hz) for **9**

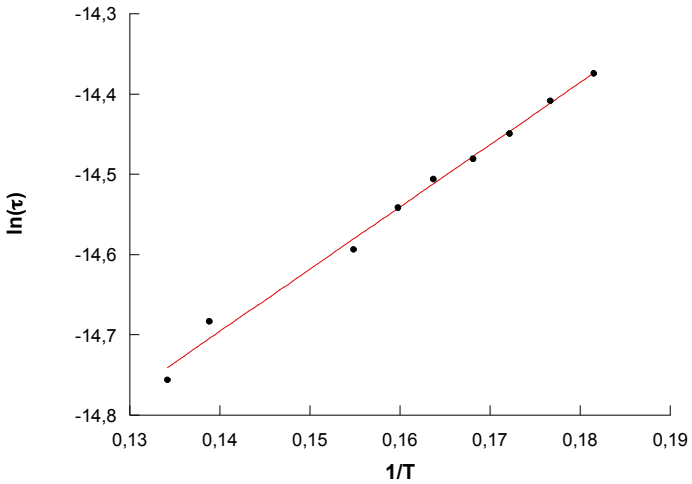

Figure *S34*: Arrhénius plot for **9**

Comparison of magnetic properties of $[Co(CuTbL^2)]_2$ (4) and $[Co(NiTbL^2)]_2$

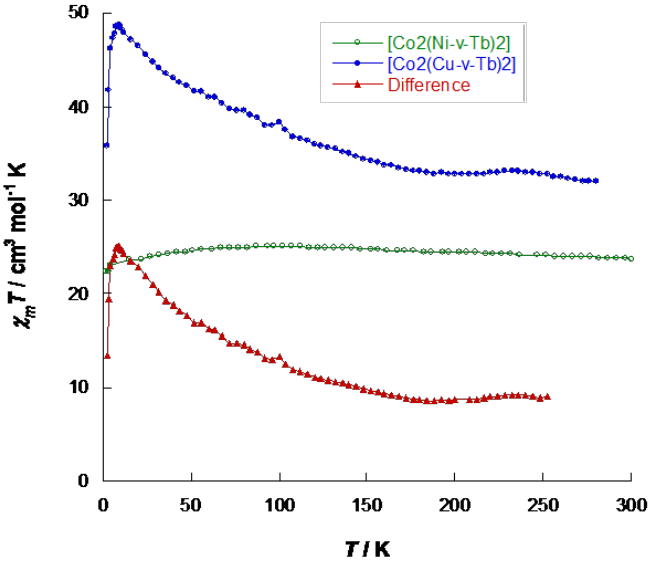

Figure *S35*: DC measurements for $[Co(CuTbL^2)]_2$ **4** and $[Co(NiTbL^2)]_2$ and the difference

$$\Delta(\chi T) = \chi T_{(CoCuTb)2} - \chi T_{(CoNiTb)2}$$

Magnetic properties of $[CuTbL^1]$ and $[CuTbL^2]$

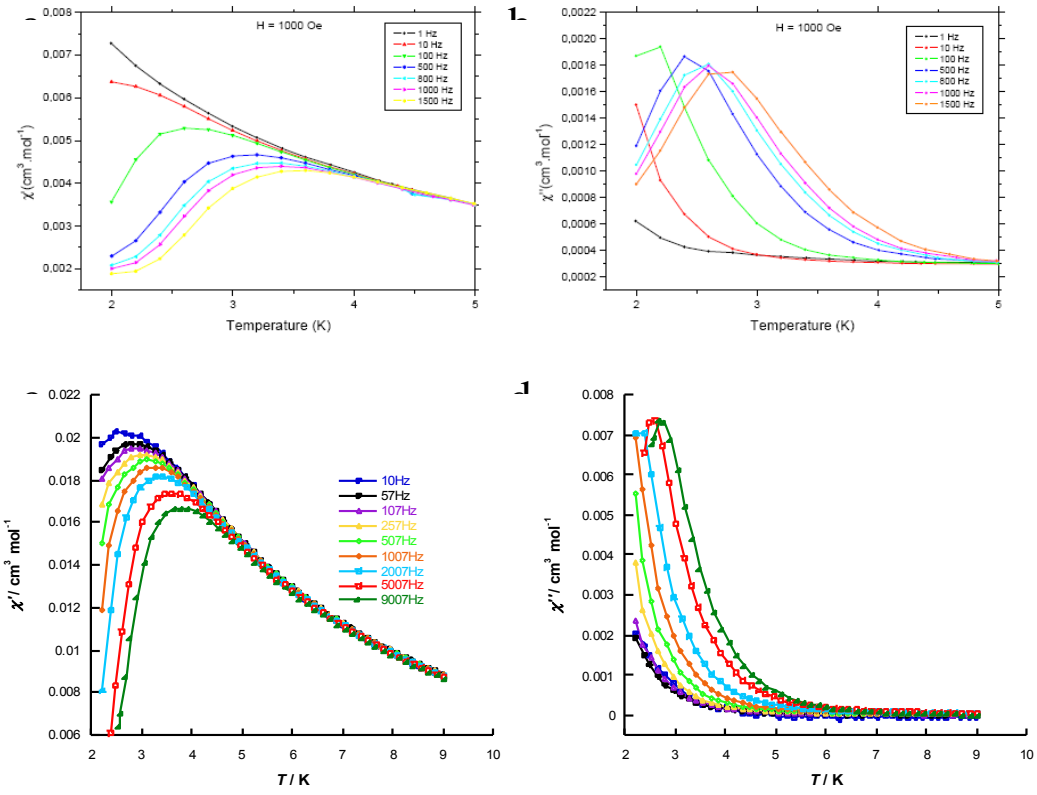

Figure *S36*: AC measurements of $[CuTbL^2]$ at 1000 Oe (10Hz – 9007 Hz) for (a and b) ; AC measurements of $[CuTbL^1]$ at 1600 Oe (10Hz – 9007 Hz) (c and d)