Supporting Information

Tetranuclear [Cu_3Ln] complexes derived from a tetraketone-type ligand

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Contents

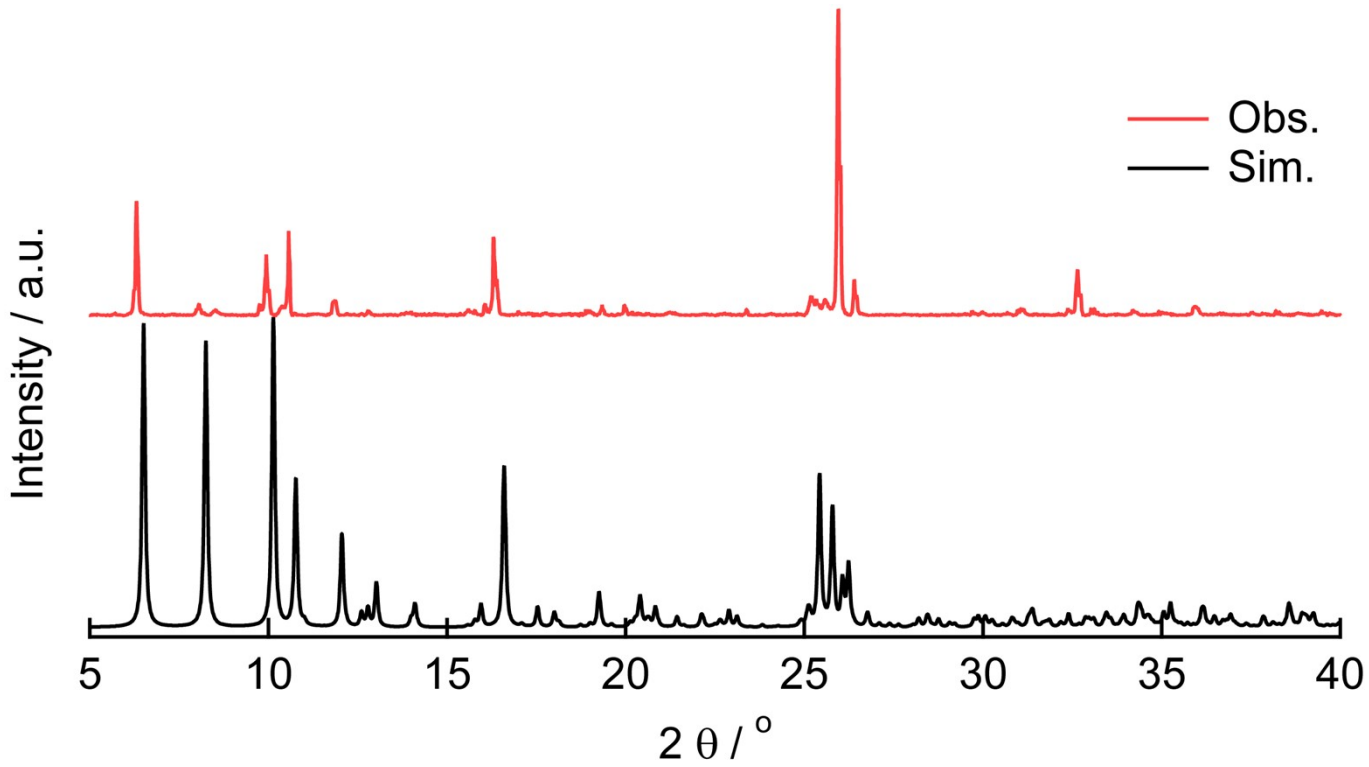

Figure S1 Experimental (red) and simulated (black) powder X-ray diffraction data of **1**'.

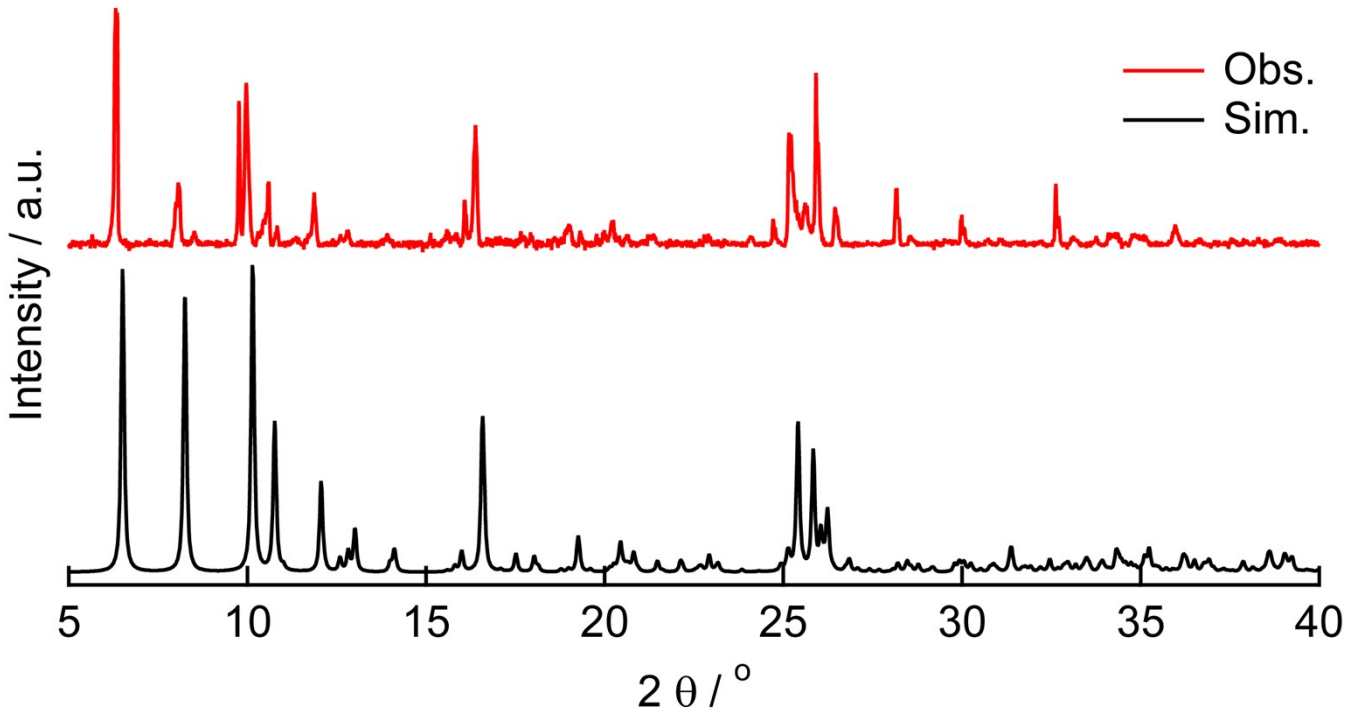

Figure S2 Experimental (red) and simulated (black) powder X-ray diffraction data of **2**'.

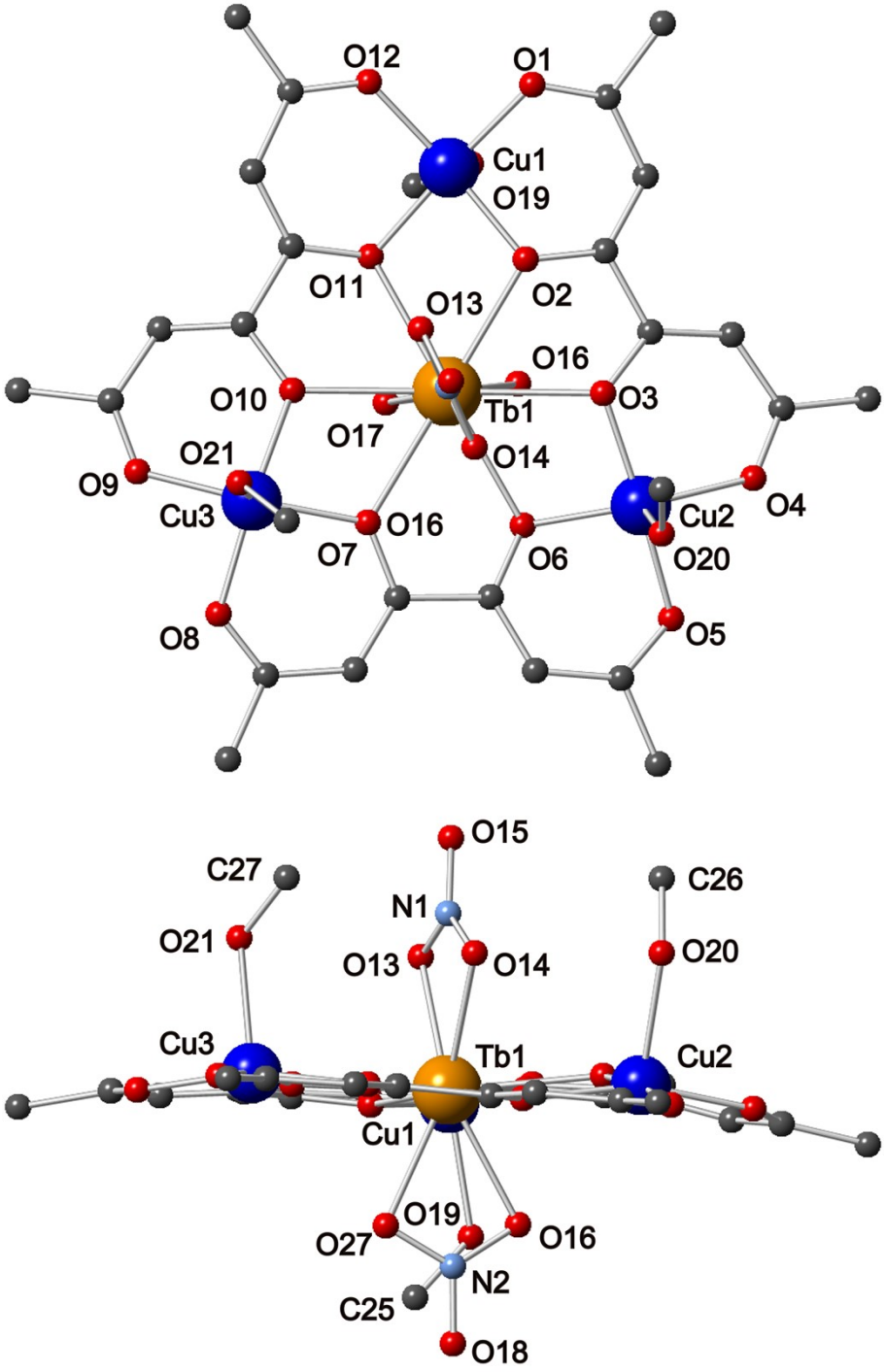

Figure S3 Molecular structures of complex **2'**. Top view (top) and side view (bottom)

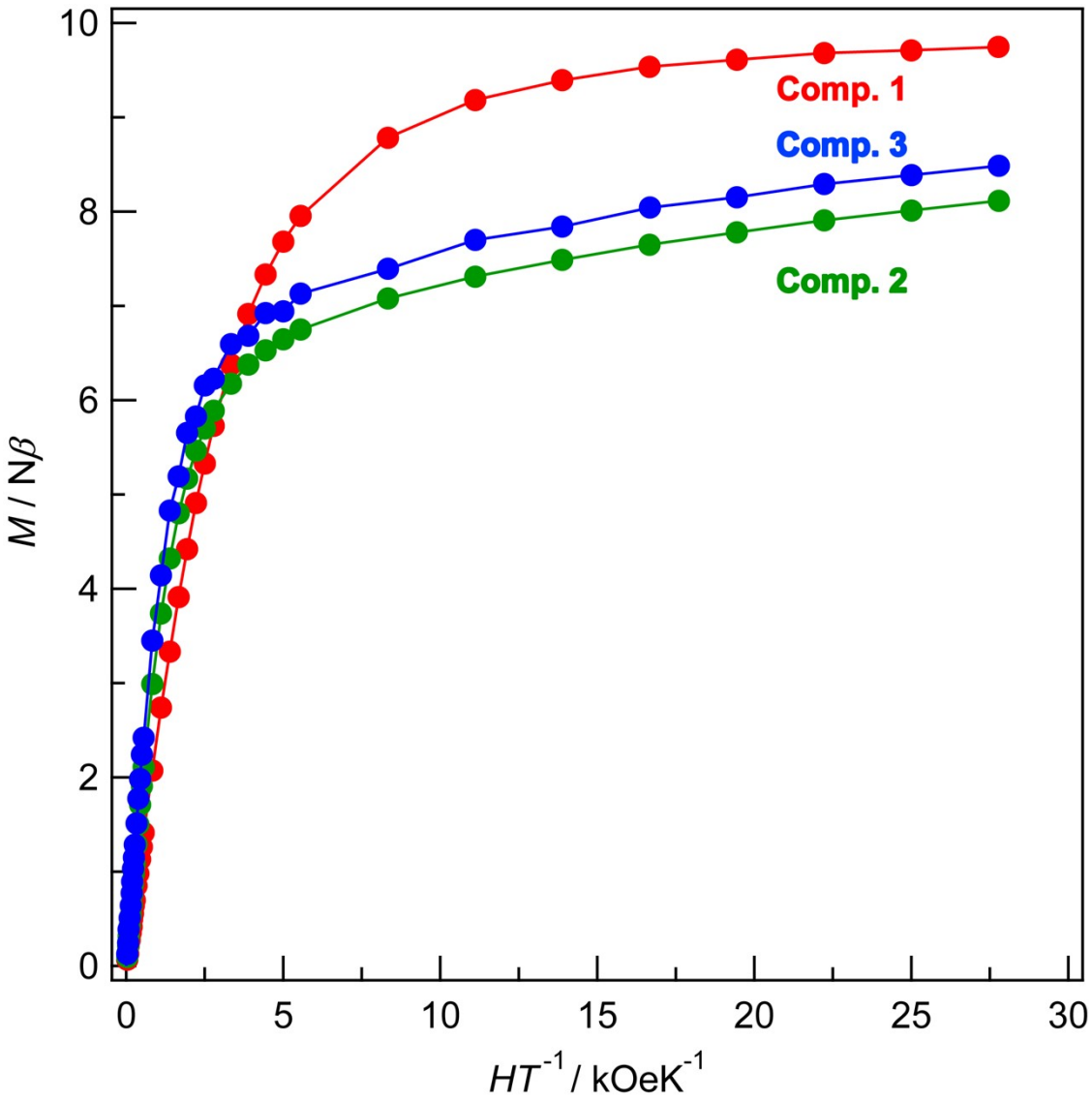

Figure S4 Field dependences of magnetization for complexes **1** (red), **2** (green), and **3** (blue).

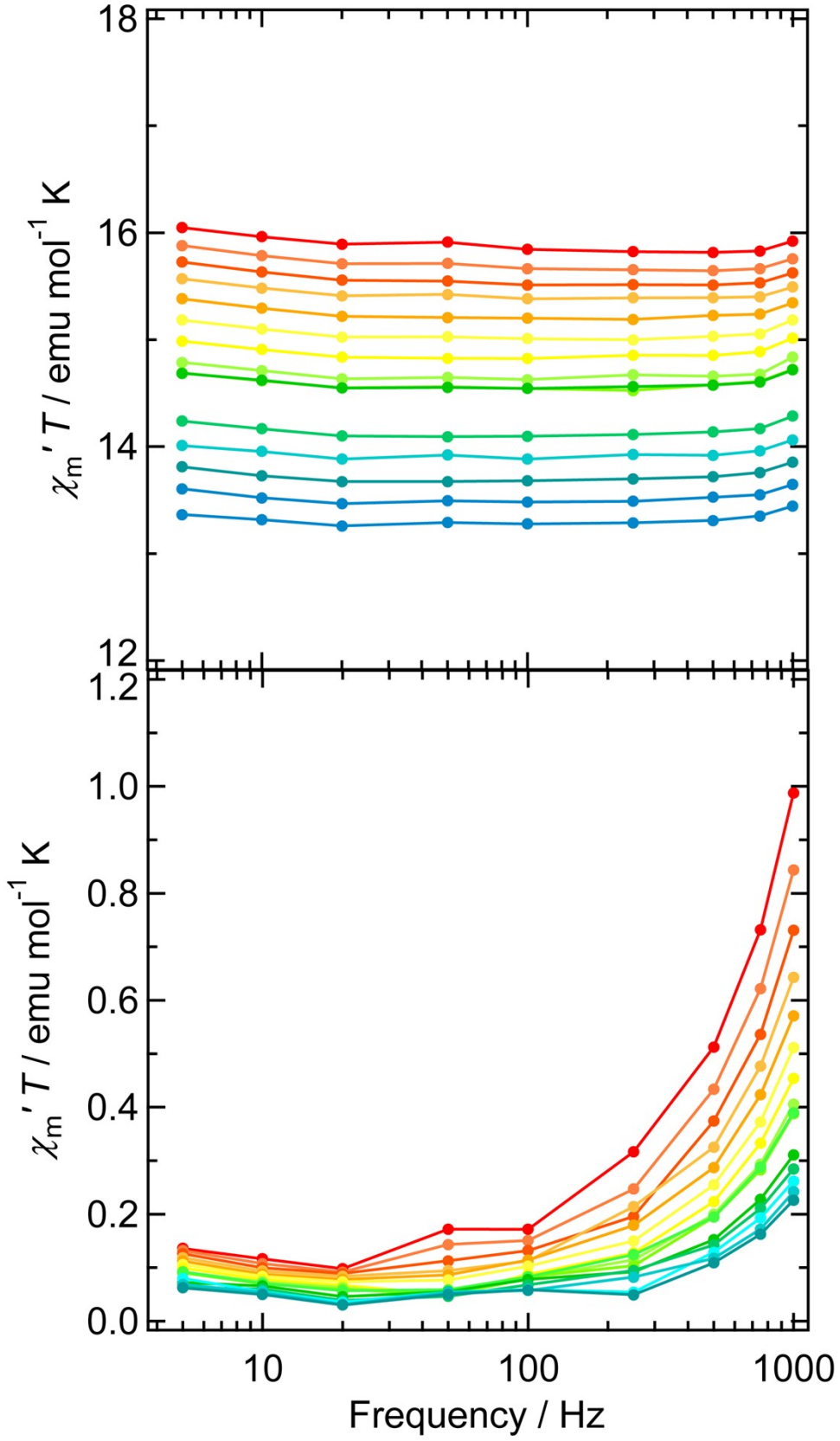

Figure S5 The AC magnetic susceptibilities of complex **3** under an applied dc magnetic field of 1300 Oe.

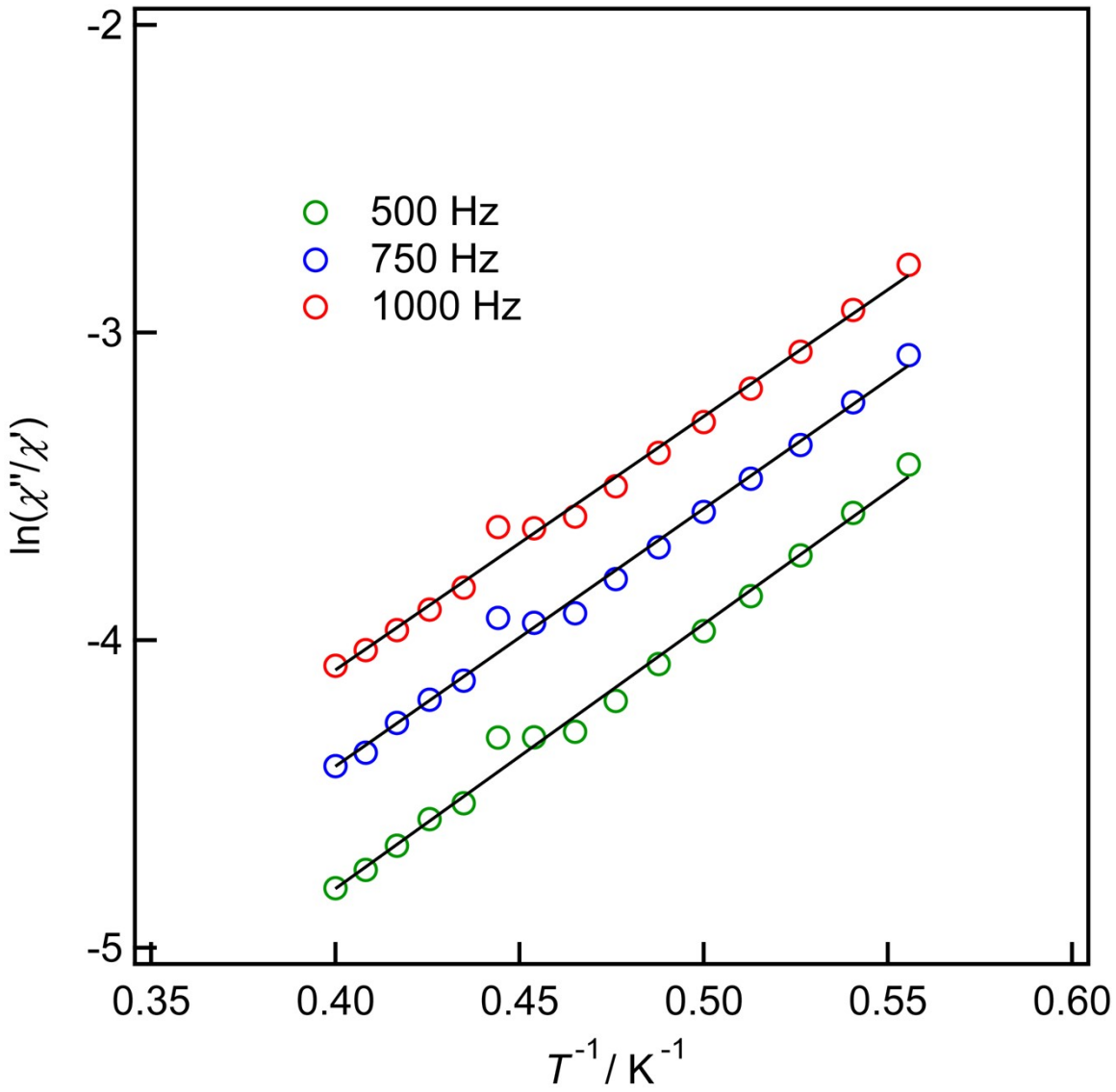

Figure S6 Debye plots of complex **3** for frequencies 1000 (red), 750 (blue), 500 (green) Hz. The solid lines correspond to the fit of the data.

Table S1. Crystal parameters of **1'**, **2'**, and **3'**.

	Comp. 1'	Comp. 2'	Comp. 3'
Formula	$C_{29}H_{44}Cu_3GdN_3O_{26}$	$C_{29}H_{44}Cu_3N_3O_{26}Tb$	$C_{27}H_{36}Cu_3DyN_3O_{24}$
M / g mol^{-1}	1198.54	1200.21	1139.71
Temp. / K	100(2)	100(2)	100(2)
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	$P2_1/c$	*P***Error!**
a / Å	8.9376(8)	8.9281(8)	7.9231(6)
b / Å	27.147(2)	27.150(2)	11.5750(10)
c / Å	17.9174(16)	17.9180(17)	22.3077(18)
α / °	–	–	93.0390(10)
β / °	103.2910(10)	103.5200(10)	91.7730(10)
γ / °	–	–	105.8840(10)
V / Å^3	4230.8(7)	4222.9(7)	1962.8(3)
Z	4	4	2
d / g cm^{-3}	1.882	1.888	1.928
μ / mm^{-1}	3.130	3.240	3.578
F(000)	2392	2396	1128
Reflections collected / unique	24193 / 9682	20642 / 7777	11429 / 8616
R_{int}	0.0312	0.0309	0.1627
GOF	1.254	1.267	1.032
$R1$ ($I > 2\sigma(I)$)	0.0558	0.0848	0.0629
R_w2 ($I > 2\sigma(I)$]	0.1223	0.1955	0.1716
$\Delta\rho_{max}$ / e Å^{-3}	1.365	3.081	6.271
$\Delta\rho_{min}$ / e Å^{-3}	–2.086	–2.742	–4.831
CCDC No.	2223281	2223282	2223283

Table S2 Maximum values of the entropy changes for the previously reported MCE materials based on Cu(II)-Gd(III) systems with up to nonanuclear clusters.

Complexes	$-\Delta S_m$ (J kg^{-1} K^{-1})	ΔH (T)	T_{max} (K)	Ref.
Cu_3Gd	16.4	5	2.4	This work
Cu_5Gd_4	31	9	3.0	1
Cu_2Gd_7	34.6	9	2.7	2
Cu_3Gd_6	26.9	7	3.0	3
Cu_6Gd_2	11.9	7	2.0	4
Cu_5Gd_2	16.3	5	2.0	5
Cu_5Gd_2	15.7	5	2.0	6
Cu_4Gd_2	22.9	7	3.0	7
Cu_4Gd	10	7	3.0	8
Cu_2Gd_2	23.5	7	3.0	9
Cu_2Gd_2	22	7	3.0	10
Cu_2Gd_2	17	7	3.0	10
Cu_2Gd	17	7	3.5	11
CuGd	23.5	7	2.3	12

References

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Explanation of alerts in CIFCHECK

Datablock: Comp1 _Cu3Gd-L1

Alert level B

The following B-level alerts arise from the diffraction data being slightly weak.
PLAT220_ALERT_2_B NonSolvent Resd 1 C Ueq(max)/Ueq(min) Range 6.4 Ratio
PLAT972_ALERT_2_B Check Calcd Resid. Dens. 1.23Ang From C9 -2.53 eA-3

Datablock: Comp2 _Cu3Tb-L1

Alert level A

The following A level alert arise from the imperfect absorption correction of heavy metal (Tb ion) compound.
PLAT971_ALERT_2_A Check Calcd Resid. Dens. 0.96Ang From Tb1 3.70 eA-3

Alert level B

The following B-level alerts arise from the diffraction data being slightly weak.
PLAT214_ALERT_2_B Atom O24 (Anion/Solvent) ADP max/min Ratio 5.3 prolat
PLAT220_ALERT_2_B NonSolvent Resd 1 C Ueq(max)/Ueq(min) Range 6.4 Ratio
PLAT415_ALERT_2_B Short Inter D-H..H-X H40 ..H42 . 1.99 Ang.
1+x,y,z = 1_655 Check
PLAT420_ALERT_2_B D-H Bond Without Acceptor O25 --H40 . Please Check
PLAT934_ALERT_3_B Number of (Iobs-Icalc)/Sigma(W) > 10 Outliers .. 2 Check

The following B level alert arise from the imperfect absorption correction of heavy metal (Tb ion) compound.
PLAT971_ALERT_2_B Check Calcd Resid. Dens. 1.79Ang From O25 2.58 eA-3
PLAT972_ALERT_2_B Check Calcd Resid. Dens. 1.09Ang From C17 -3.31 eA-3
PLAT972_ALERT_2_B Check Calcd Resid. Dens. 1.59Ang From C8 -2.86 eA-3

Datablock: Comp3 _Cu3Dy-L1

Alert level A
The following A level alert arise from the imperfect absorption correction of heavy metal (Dy ion) compound.
PLAT971_ALERT_2_A Check Calcd Resid. Dens. 0.89Ang From Dy1 6.31 eA-3
PLAT971_ALERT_2_A Check Calcd Resid. Dens. 0.77Ang From Dy1 5.73 eA-3
PLAT972_ALERT_2_A Check Calcd Resid. Dens. 0.85Ang From Dy1 -4.98 eA-3
PLAT972_ALERT_2_A Check Calcd Resid. Dens. 0.85Ang From Dy1 -4.79 eA-3
PLAT972_ALERT_2_A Check Calcd Resid. Dens. 0.74Ang From Dy1 -4.41 eA-3
PLAT972_ALERT_2_A Check Calcd Resid. Dens. 0.67Ang From Dy1 -4.23 eA-3

Alert level B

The following B-level alerts arise from the diffraction data being slightly weak.

PLAT213_ALERT_2_B Atom O6 has ADP max/min Ratio ..... 4.1 prolat
PLAT213_ALERT_2_B Atom O7 has ADP max/min Ratio ..... 4.4 prolat
PLAT213_ALERT_2_B Atom O10 has ADP max/min Ratio ..... 5.0 prolat
PLAT213_ALERT_2_B Atom C14 has ADP max/min Ratio ..... 4.2 prolat

The following B level alert arise from the imperfect absorption correction of heavy metal (Dy ion) compound.

PLAT971_ALERT_2_B Check Calcd Resid. Dens. 0.96Ang From Dy1 2.70 eA-3
PLAT971_ALERT_2_B Check Calcd Resid. Dens. 1.01Ang From O19 2.56 eA-3
PLAT972_ALERT_2_B Check Calcd Resid. Dens. 1.39Ang From Dy1 -3.01 eA-3
PLAT972_ALERT_2_B Check Calcd Resid. Dens. 1.37Ang From Dy1 -3.01 eA-3