Supporting Information

A series of hetero-multi-spin Ln_2Cu_3 complexes based on a methyl-pyrazole nitronyl nitroxide radical with slow magnetic relaxation behaviors

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1. Crystallographic Data

X-Ray crystallography. Crystallographic data were measured at 150 K (for **1**) 293 K (for **2**) and 150 K (for **3**) on an Agilent SuperNova (Dual, Cu at zero, AtlasS2, CCD) diffractometer equipped with graphite-monochromated Cu-Kα radiation (λ = 1.54184 Å), using the *φ*–*ω* scan technique. Semiempirical multiscan absorption corrections were applied by SCALE3 ABSPACK, and the programs CrysAlisPro were used for integration of the diffraction profiles.[1] The structures were solved by direct methods and refined using least squares minimization using the ShelXT and ShelXL programs.[2] Some restraints are employed, such as ISOR (anisotropic parameter), DFIX (restricting the distance between two atoms) to solve the disorder of the F atoms. Besides F atoms, all other non-hydrogen atoms were refined anisotropically, and hydrogen atoms were located geometrically and refined isotropically. Crystallographic data for the three compounds are listed in Table S1.

Table S1. Crystallographic Data and Structure Refinement Details for **1-3**

	1	**2**	**3**
formula	$C_{52}H_{40}Cu_{1.5}F_{36}GdN_8O_{16}$	$C_{52}H_{40}Cu_{1.5}F_{36}N_8O_{16}Tb$	$C_{52}H_{40}Cu_{1.5}DyF_{36}N_8O_{16}$
Mr	1969.48	1971.15	1974.73
crystal system	triclinic	triclinic	triclinic
space group	*P*$\bar{1}$	*P*$\bar{1}$	*P*$\bar{1}$
a (Å)	11.9296(3)	11.9225(2)	11.9061(2)
b (Å)	18.3338(3)	18.3300(3)	18.3248(5)
c (Å)	20.3498(4)	20.3485(4)	20.3320(5)
α(°)	94.2310(10)	94.5361(15)	94.322(2)
β(°)	92.598(2)	92.4970(15)	92.4181(17)
γ(°)	95.684(2)	95.6302(15)	95.6122(19)
V (Å^3)	4410.63(16)	4405.71(14)	4396.67(19)
Z	2	2	2
*ρ*calc (Mg/m^3)	1.483	1.486	1.492
μ (mm^{-1})	6.443	5.528	6.131
F(000)	1935	1937	1939
θ range(°)	3.135~67.077	2.181~67.079	2.182~67.078
GOF on F^2	1.083	1.023	0.998
R_1/wR_2[$I > 2\sigma(I)$]	0.0714, 0.2003	0.0439, 0.1123	0.0665, 0.1664
R_1/wR_2 (all data)	0.0781, 0.2100	0.0465, 0.1146	0.0773, 0.1759

2. Powder X-ray Diffraction

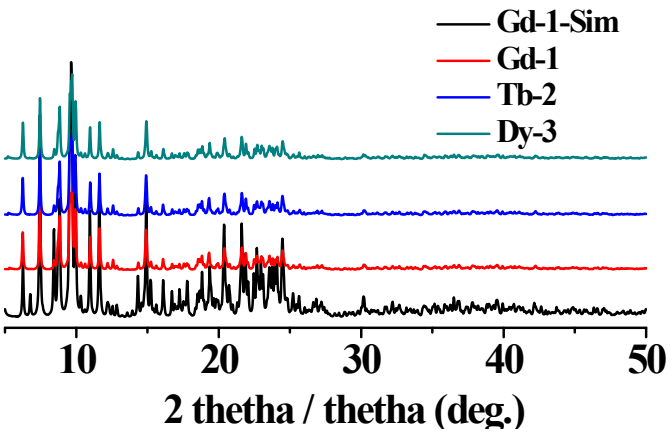

Figure S1. Powder X-ray diffractions of **1-3**.

3. Other crystal structure graphic

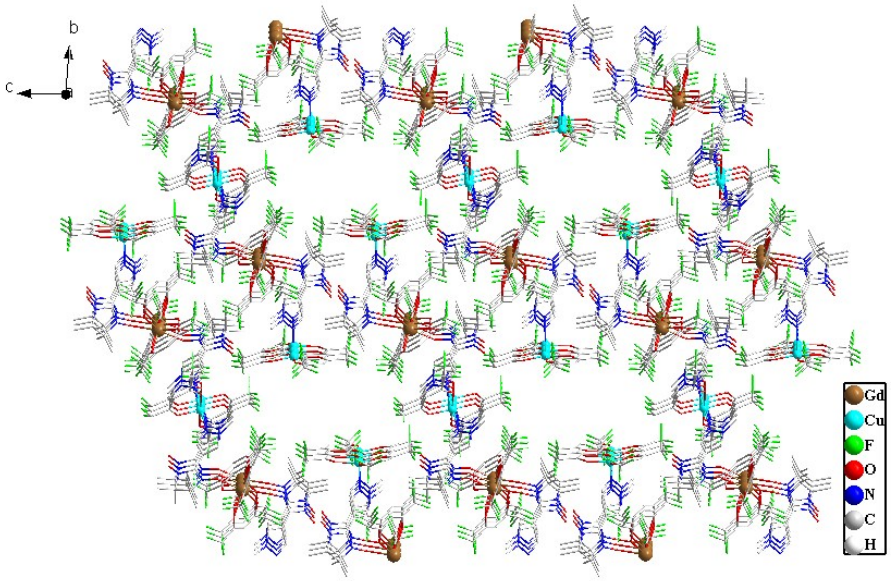

Figure S2. Packing arrangement of the clusters in **1**. Hydrogen atoms are omitted for clarity.

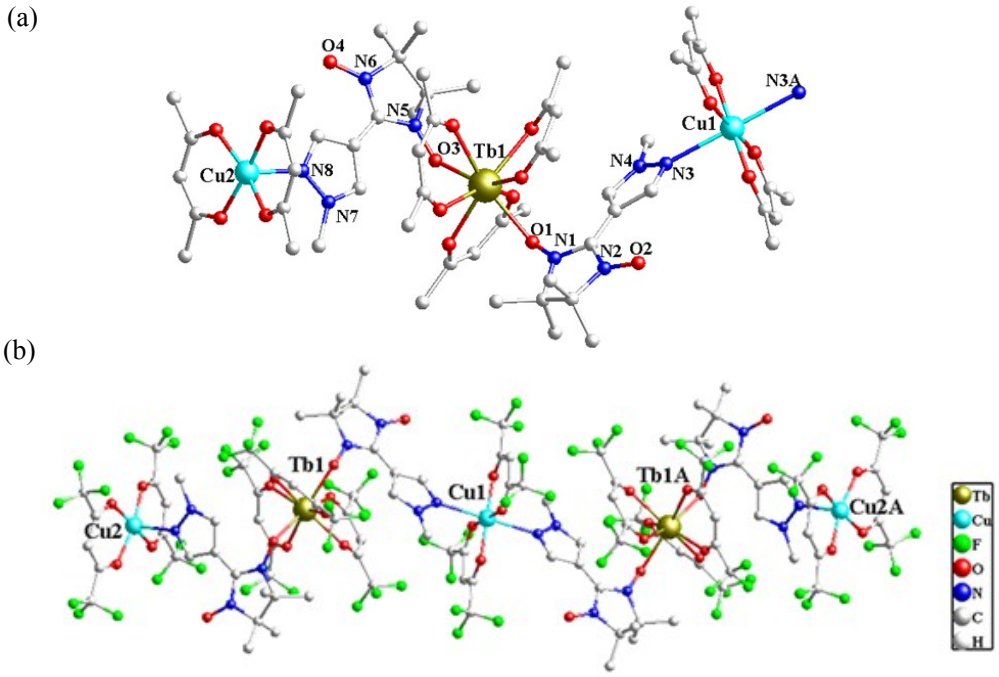

Figure S3. (a) The asymmetry unit of $[Tb_2Cu_3(hfac)_{12}(4\text{-NIT-MePyz})_4]$ (**2**). Fluorine and hydrogen atoms are omitted for clarity. (b) The detail arrangement of the Tb_2Cu_3 cluster in **2**.

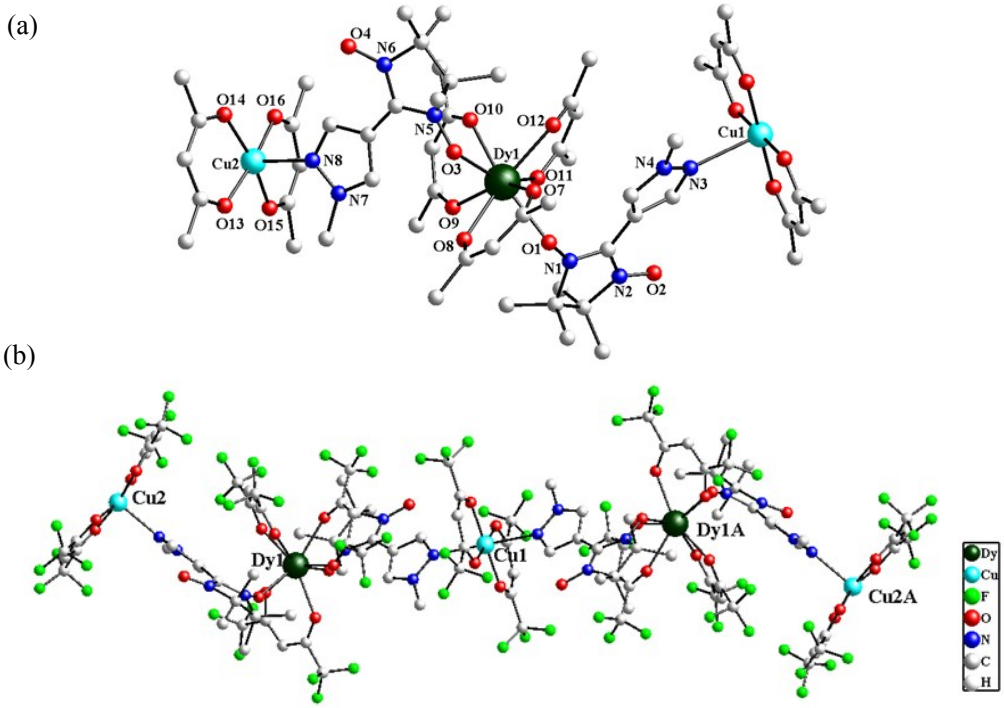

Figure S4. (a) The asymmetry unit of $[Dy_2Cu_3(hfac)_{12}(4\text{-NIT-MePyz})_4]$ (**3**). Fluorine and hydrogen atoms are omitted for clarity. (b) The detail arrangement of the Dy_2Cu_3 cluster in **3**.

Table S2. Lanthanide geometry analysis by *SHAPE* software

Ln(III)	D_{2d}-DD	C_{2v}-TP	D_{4d}-AP
Gd1(**1**)	0.123	2.500	2.267
Tb1(**2**)	0.111	2.514	2.243
Dy1(**3**)	0.099	2.508	2.285

4. Other magnetic data

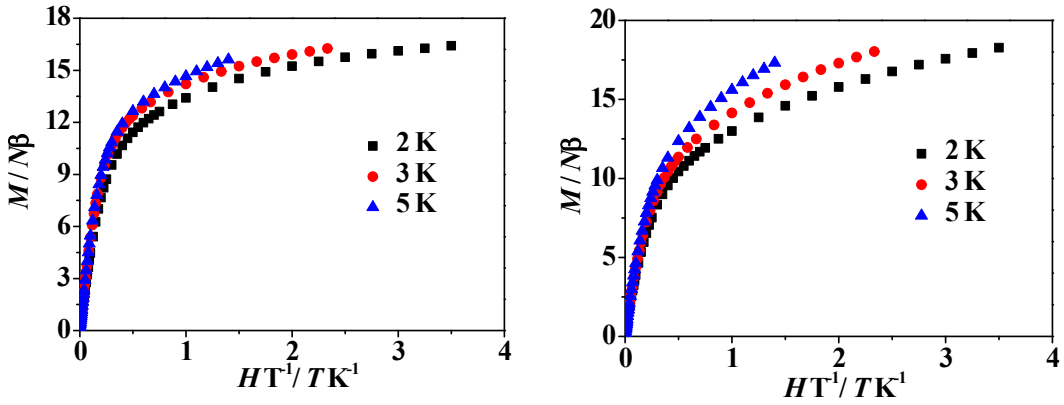

Figure S5. Field dependence of the magnetization at the temperature of 2, 3, and 5 K for complexes **2** (left) and **3** (right).

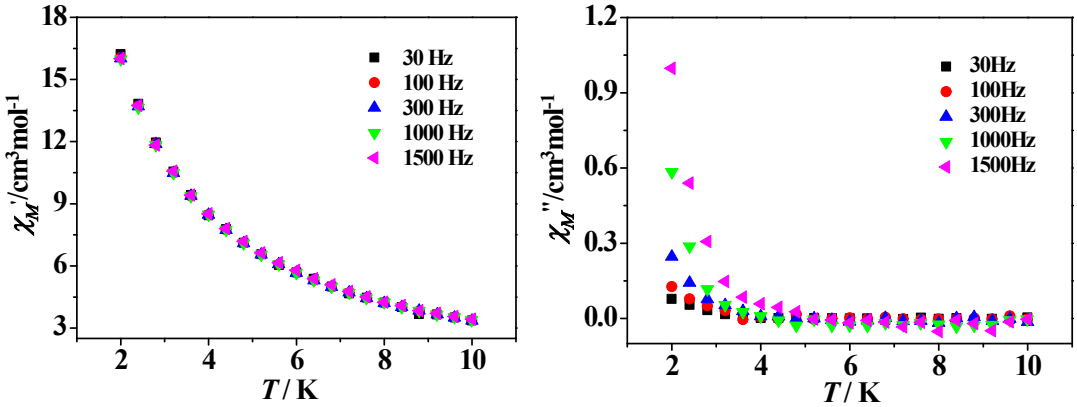

Figure S6. Temperature dependencies of the in-phase (left) and out-phase (right) components of the ac magnetic susceptibility for **2** at zero dc fields with an oscillation of 3.0 Oe at frequencies from 30 Hz to 10000 Hz.

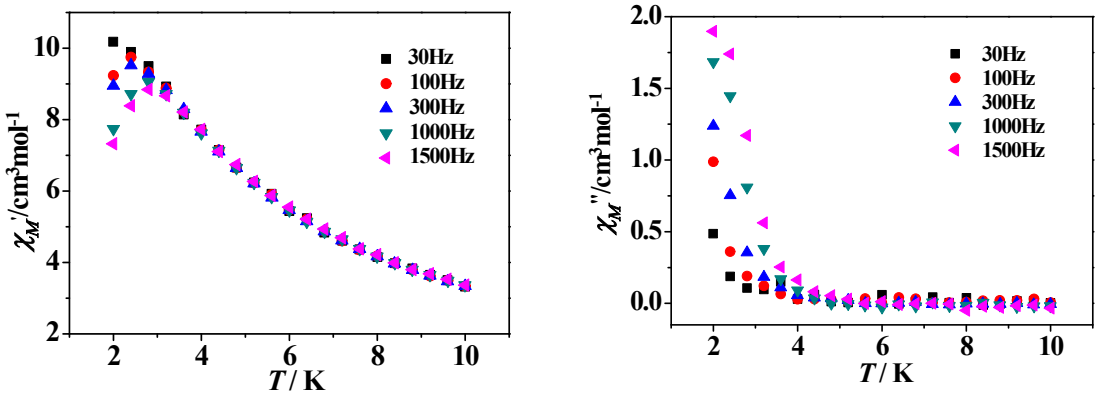

Figure S7. Temperature dependencies of the in-phase (left) and out-phase (right) components of the ac magnetic susceptibility for **2** at 2000 Oe dc fields with an oscillation of 3.0 Oe at frequencies from 30 Hz to 1500 Hz.

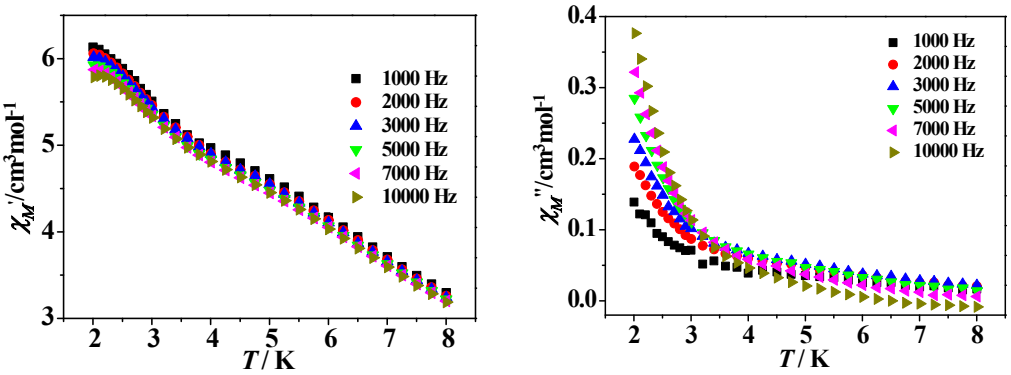

Figure S8. Temperature-dependent of the in-phase (χ', left) and out-of-phase signals (χ'', right) components of the ac magnetic susceptibility for **3** under 2000 Oe dc fields with an oscillation of 3.5 Oe at frequencies from 1000 Hz to 10000 Hz.

5. Tables of Crystal Data

Table S3. Selected bond lengths (Å) and bond angles (°) in complex **1**.

Gd(1)-O(1)	2.382(3)	O(3)-Gd(1)-O(8)	149.21(13)
Gd(1)-O(3)	2.354(4)	O(3)-Gd(1)-O(9)	72.27(14)
Gd(1)-O(7)	2.373(4)	O(3)-Gd(1)-O(10)	73.07(13)
Gd(1)-O(8)	2.370(4)	O(3)-Gd(1)-O(12)	99.07(14)
Gd(1)-O(9)	2.381(4)	O(7)-Gd(1)-O(8)	72.68(13)
Gd(1)-O(10)	2.379(4)	O(7)-Gd(1)-O(12)	136.12(14)
Gd(1)-O(11)	2.419(4)	O(8)-Gd(1)-O(12)	73.95(14)
Gd(1)-O(12)	2.352(4)	O(9)-Gd(1)-O(7)	150.90(14)
Cu(1)-O(5)	1.950(4)	O(9)-Gd(1)-O(8)	130.35(13)
Cu(1)-O(6)	1.967(4)	O(9)-Gd(1)-O(12)	72.75(14)
Cu(1)-N(3)	2.432(5)	O(10)-Gd(1)-O(7)	77.57(14)
Cu(1)-O(5)#1	1.950(4)	O(10)-Gd(1)-O(8)	128.65(13)
Cu(1)-O(6)#1	1.967(4)	O(10)-Gd(1)-O(9)	73.67(14)
Cu(1)-N(3)#1	2.432(5)	O(5)-Cu(1)-O(5)#1	180.0
Cu(2)-O(13)	1.945(4)	O(5)-Cu(1)-N(3)#1	86.48(16)
Cu(2)-O(14)	1.949(5)	O(5)-Cu(1)-N(3)	93.52(16)
Cu(2)-O(15)	1.935(5)	O(6)-Cu(1)-O(5)	92.85(16)
Cu(2)-O(16)	1.938(4)	O(6)-Cu(1)-O(5)#1	87.15(16)
Cu(2)-N(8)	2.262(5)	O(6)-Cu(1)-O(6)#1	180.0
O(1)-Gd(1)-O(3)	136.73(13)	O(6)-Cu(1)-N(3)	88.98(17)
O(1)-Gd(1)-O(7)	101.08(13)	O(13)-Cu(2)-O(14)	91.5(2)
O(1)-Gd(1)-O(8)	74.03(13)	O(13)-Cu(2)-O(15)	166.5(2)
O(1)-Gd(1)-O(9)	74.18(13)	O(13)-Cu(2)-O(16)	88.18(18)
O(1)-Gd(1)-O(10)	71.85(13)	O(13)-Cu(2)-N(8)	93.43(19)
O(1)-Gd(1)-O(12)	96.23(13)	O(14)-Cu(2)-O(16)	171.2(2)
O(3)-Gd(1)-O(7)	95.28(14)	O(15)-Cu(2)-N(8)	100.04(19)

Table S4. Selected bond lengths (Å) and bond angles (°) in complex **2**.

Tb(1)-O(1)	2.354(2)	O(3)-Tb(1)-O(8)	72.36(8)
Tb(1)-O(3)	2.354(2)	O(3)-Tb(1)-O(9)	149.24(8)
Tb(1)-O(7)	2.363(2)	O(3)-Tb(1)-O(10)	95.13(8)
Tb(1)-O(8)	2.364(2)	O(3)-Tb(1)-O(12)	73.18(8)
Tb(1)-O(9)	2.361(2)	O(7)-Tb(1)-O(8)	74.03(8)
Tb(1)-O(10)	2.359(2)	O(7)-Tb(1)-O(12)	131.77(8)
Tb(1)-O(11)	2.337(2)	O(8)-Tb(1)-O(12)	124.97(8)
Tb(1)-O(12)	2.400(2)	O(9)-Tb(1)-O(7)	128.70(8)
Cu(1)-O(5)	1.960(2)	O(9)-Tb(1)-O(8)	130.29(8)
Cu(1)-O(6)	1.959(2)	O(9)-Tb(1)-O(12)	76.21(8)
Cu(1)-N(3)	2.429(3)	O(10)-Tb(1)-O(7)	77.16(8)
Cu(1)-O(5)#1	1.960(2)	O(10)-Tb(1)-O(8)	150.87(8)
Cu(1)-O(6)#1	1.959(2)	O(10)-Tb(1)-O(9)	72.77(8)
Cu(1)-N(3)#1	2.429(3)	O(5)-Cu(1)-O(5)#1	180.00(11)
Cu(2)-O(13)	1.937(3)	O(5)-Cu(1)-N(3)#1	89.23(10)
Cu(2)-O(14)	1.945(3)	O(5)-Cu(1)-N(3)	90.77(10)
Cu(2)-O(15)	1.941(3)	O(6)-Cu(1)-O(5)	92.55(10)
Cu(2)-O(16)	1.956(3)	O(6)-Cu(1)-O(5)#1	87.45(10)
Cu(2)-N(8)	2.272(3)	O(6)-Cu(1)-O(6)#1	180.0
O(1)-Tb(1)-O(3)	136.82(8)	O(6)-Cu(1)-N(3)	86.36(10)
O(1)-Tb(1)-O(7)	72.32(8)	O(13)-Cu(2)-O(14)	92.37(11)
O(1)-Tb(1)-O(8)	74.24(8)	O(13)-Cu(2)-O(15)	172.40(13)
O(1)-Tb(1)-O(9)	73.91(8)	O(13)-Cu(2)-O(16)	87.65(11)
O(1)-Tb(1)-O(10)	101.05(8)	O(13)-Cu(2)-N(8)	95.01(12)
O(1)-Tb(1)-O(12)	149.92(8)	O(14)-Cu(2)-O(16)	166.88(12)
O(3)-Tb(1)-O(7)	72.76(8)	O(15)-Cu(2)-N(8)	92.59(12)

Table S5. Selected bond lengths (Å) and bond angles (°) in complex **3**.

Dy(1)-O(1)	2.345(3)	O(3)-Dy(1)-O(8)	72.38(13)
Dy(1)-O(3)	2.348(3)	O(3)-Dy(1)-O(9)	99.19(13)
Dy(1)-O(7)	2.355(4)	O(3)-Dy(1)-O(10)	73.07(13)
Dy(1)-O(8)	2.349(4)	O(3)-Dy(1)-O(12)	95.33(13)
Dy(1)-O(9)	2.324(4)	O(7)-Dy(1)-O(8)	74.20(14)
Dy(1)-O(10)	2.395(4)	O(7)-Dy(1)-O(12)	76.98(14)
Dy(1)-O(11)	2.358(3)	O(8)-Dy(1)-O(12)	150.89(13)
Dy(1)-O(12)	2.348(4)	O(9)-Dy(1)-O(7)	146.94(13)
Cu(1)-O(5)	1.962(4)	O(9)-Dy(1)-O(8)	72.83(13)
Cu(1)-O(6)	1.962(3)	O(9)-Dy(1)-O(12)	136.08(13)
Cu(1)-N(3)	2.430(5)	O(10)-Dy(1)-O(7)	131.42(13)
Cu(1)-O(5)#1	1.962(4)	O(10)-Dy(1)-O(8)	150.87(8)
Cu(1)-O(6)#1	1.962(3)	O(10)-Dy(1)-O(9)	72.32(13)
Cu(1)-N(3)#1	2.430(5)	O(5)-Cu(1)-O(5)#1	180.0
Cu(2)-O(13)	1.938(4)	O(5)-Cu(1)-N(3)#1	88.90(16)
Cu(2)-O(14)	1.954(4)	O(5)-Cu(1)-N(3)	91.10(16)
Cu(2)-O(15)	1.946(4)	O(6)-Cu(1)-O(5)	92.76(15)
Cu(2)-O(16)	1.943(4)	O(6)-Cu(1)-O(5)#1	87.24(15)
Cu(2)-N(8)	2.268(5)	O(6)-Cu(1)-O(6)#1	180.0
O(1)-Dy(1)-O(3)	137.27(13)	O(6)-Cu(1)-N(3)	86.21(15)
O(1)-Dy(1)-O(7)	72.72(13)	O(13)-Cu(2)-O(14)	92.09(19)
O(1)-Dy(1)-O(8)	74.42(12)	O(13)-Cu(2)-O(15)	85.94(19)
O(1)-Dy(1)-O(9)	95.92(13)	O(13)-Cu(2)-O(16)	171.8(2)
O(1)-Dy(1)-O(10)	149.59(13)	O(13)-Cu(2)-N(8)	92.9(2)
O(1)-Dy(1)-O(12)	100.90(13)	O(14)-Cu(2)-O(16)	87.41(17)
O(3)-Dy(1)-O(7)	72.92(13)	O(15)-Cu(2)-N(8)	99.93(18)

6. References

(1) O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr*. **2009**, *42*, 339–341.

(2) (*a*) G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Adv.* 2015, **71**, 3–8; (*b*) G. M. Sheldrick, *Acta Crystallogr., Sect. C: Struct. Chem.* 2015, **71**, 3–8.