Supporting Information

Novel three-dimensional 3*d*-4*f* microporous magnets exhibiting selective gas adsorption behavior†

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Experimental Section:

Materials and Physical Measurements. The reagents and solvents employed were commercially available and used as received without further purification. The C, H, and N microanalyses were carried out with an Elementar Vario-EL CHNS elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range 4000-400 cm^{-1} on a Bio-Rad FTS-7 spectrometer. X-ray powder diffraction (XRD) intensities for **1**-**3** were measured at 293 K on a Rigaku D/max-IIIA diffratometer (Cu-K_α, λ= 1.54056 Å). The crushed single-crystalline powder samples were prepared by crushing the crystals and scanned from 5-60^o with a step of 0.4^o/s. Calculated patterns of **1**-**3** were generated with Mercury. TG data were obtained on a TG209F3 Tarsus thermogravimetry, with a heating rate of 10 °C min^{-1} in an air atmosphere. The magnetic measurements were carried out with Quantum Design SQUID MPMS XL-7 instruments. The diamagnetism of the sample and sample holder were taken into account. Measurements for the gas adsorption isotherms of N_2 (77 K), H_2 (77 K), and CO_2 (195 K), were performed in the gaseous state by using BELSORP-max volumetric adsorption equipment from BEL Japan. Gases are highly pure and a 98.3 mg crystal powder sample of desolvated **1** was used for all the three measurements.

Hydrothermal Synthesis.

$[Sm_4Co_3(pyta)_6(H_2O)_9]\cdot 5H_2O$ (**1**) A mixture of $Sm(NO_3)_3\cdot 6H_2O$ (0.1 mmol, 0.041 g), $Co(NO_3)_2.6H_2O$ (0.25 mmol, 0.084 g) and H_3pyta (0.5 mmol, 0.105 g) and distilled H_2O (10 mL) was sealed in a 23-mL Teflon-liner autoclave. Heated in an oven to 185 ^{o}C for 96 hs, and then cooled to room temperature at a rate of 5 ^{o}C h^{-1}, yielded orange cuboid crystals of **1** (yields 30 mg, calcd. 53 %, based on Sm) Elemental analysis calcd. (%) for $C_{48}H_{40}Co_3Sm_4N_6O_{50}$: C 25.30, H 1.77, N 3.69; Found: C 24.99, H 2.384, N 3.531; IR (4000 – 400 cm^{-1}): 3386 m, 3079 w, 1616 s, 1440 m, 1377 s, 1281 m, 1230 w, 1113 w, 1033 w, 945 w, 785 m, 756 m, 708 m;

$[Eu_4Co_3(pyta)_6(H_2O)_9]\cdot 5H_2O$ (**2**) The procedure was the same as that for **1** except that $Eu(NO_3)_3\cdot 6H_2O$ was used instead of $Sm(NO_3)_3\cdot 6H_2O$, giving orange cuboid crystals of **2.** (yields 12 mg, calcd. 21 %, based on Eu). Elemental analysis calcd. (%) for $C_{48}H_{40}Co_3Eu_4N_6O_{50}$: C 25.22, H 1.76, N 3.68; Found: C

24.84, H 2.386, N 3.786 IR (4000 – 400 cm^{-1}): 3393 m, 3081 w, 1615 s, 1440 m, 1377 s, 1279 m, 1230 w, 1113 w, 1033 w, 940 w, 782 m, 755 m, 706 m;

$[Gd_4Co_3(pyta)_6(H_2O)_9]\cdot 8H_2O$ (**3**) The procedure was the same as that for **1** except that $Gd(NO_3)_3\cdot 6H_2O$ was used instead of $Sm(NO_3)_3\cdot 6H_2O$, giving orange cuboid crystals of **3** (yields 8 mg, calcd. 14 %, based on Gd) Elemental analysis calcd. (%) for $C_{48}H_{40}Co_3Gd_4N_6O_{50:}$ C 24.99, H 1.75, N 3.64; Found: C 24.40, H 2.543, N 3.669; IR (4000 – 400 cm^{-1}): 3389 m, 3076 w, 1606 s, 1435 m, 1371 s, 1277 m, 1230 w, 1113 w, 1033 w, 940 w, 782 m, 759 m, 711 m;

X-Ray Crystallography.

Single crystal diffraction intensities of **2** were collected on a Bruker Apex CCD area-detector diffractometer (Mo-Kα, λ = 0.71073 Å). Absorption corrections were applied by using multiscan program SADABS.[1] The structures were solved with direct method and refined with full-matrix least-squares technique with the SHELXTL program package.[2] Anisotropic thermal parameters were applied to all non-hydrogen atoms. The organic hydrogen atoms were generated geometrically (C-H 0.93 Å). The hydrogen atoms of the aqua ligands as well as the lattice water molecules in **2** were not located from difference maps or calculated. For the refinements of the disordered O4w, O5w, O6w and O7w in **2**, they were modeled as variable occupancy oxygen atoms of water molecules, and the occupancies were allowed to refine freely and subsequently fixed near the final refined values (treated as each occupation of 50%). Several restraints were employed to restrain the thermal vibrations of O1 O9 O3W O4W O5W O6W O7W O10W. Selected bond lengths and bond angles are listed in Table S1.

Cell parameters for **1**: monoclinic, *C*2/*c* , a = 21.042(3) Å, b = 20.225(3) Å, c = 18.068(2) Å, β = 118.601(2)°, V = 6750.7(15) $Å^3$. For **3**: monoclinic, *C*2/*c*, a = 20.902(5) Å, b = 20.251(5) Å, c = 18.055(4) Å, β = 118.48(2)°, V = 6717.1(10) $Å^3$.

References:

1 G. M. Sheldrick, *SADABS 2.05*, University of Göttingen.

2 *SHELXTL 6.10*, Bruker Analytical Instrumentation, Madison, Wisconsin, USA, 2000.

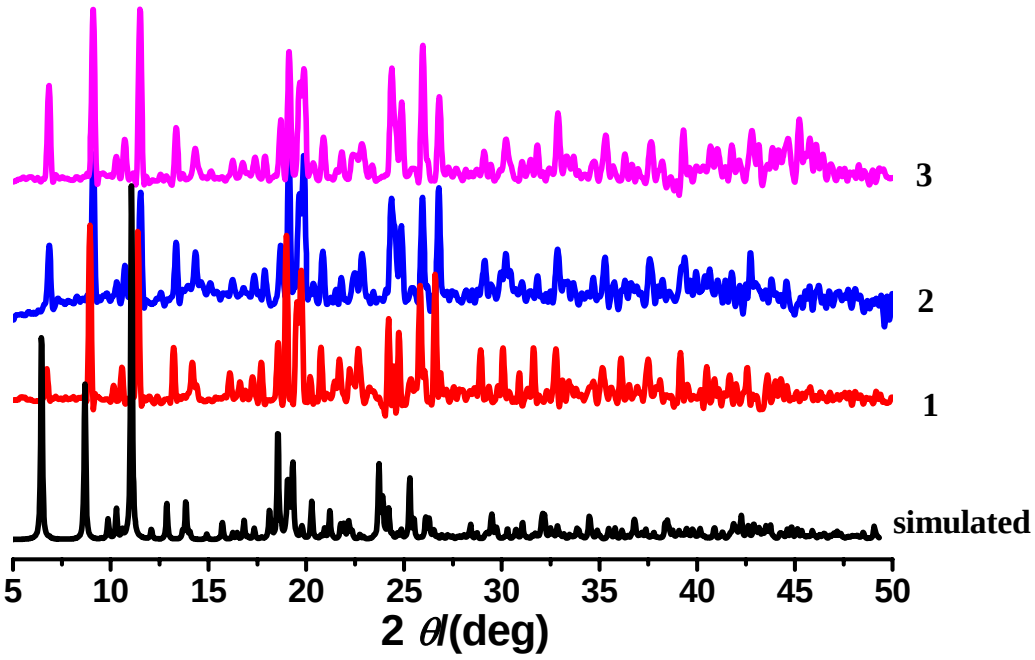


Fig. S1 XRD patterns of **1** (red), **2** (blue) and **3** (magenta).

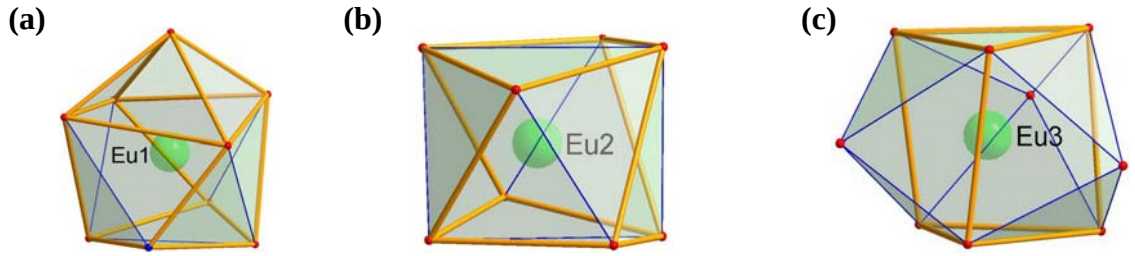


Fig. S2 Coordination polyhedrons of Eu atoms in **2.**

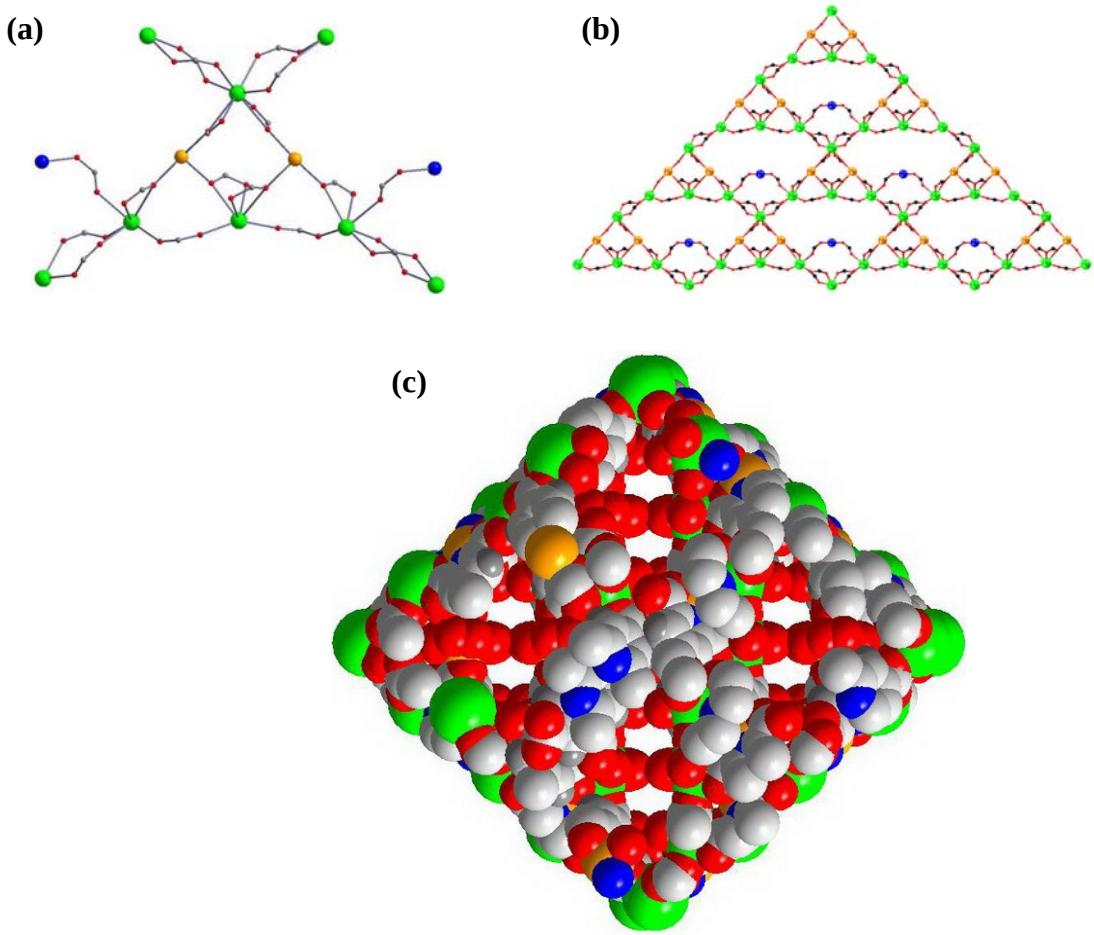


Fig. S3 (a) $Eu_4Co_2(COO)_{18}$ unit linked four vertex Eu and two Co2 atoms (b) 2D layer in *ab* plane constructed from Eu, Co1, Co2 atoms and carboxylate groups in **2**. (c) Space- filling mode of 3D MOF of **2** viewed down from *c* axis. Guest water molecules in the channels are omitted for clarity. Green, Eu; yellow, Co1; blue, Co2; red, O; black, C.

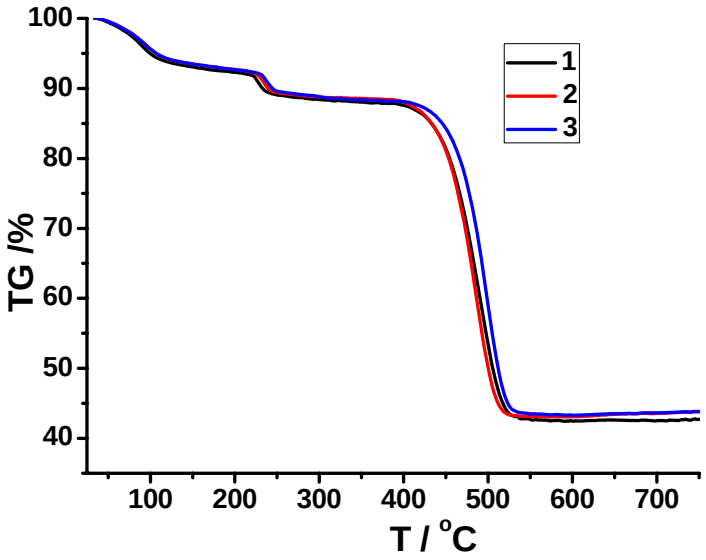


Fig. S4. TG curve of **1-3** under air.

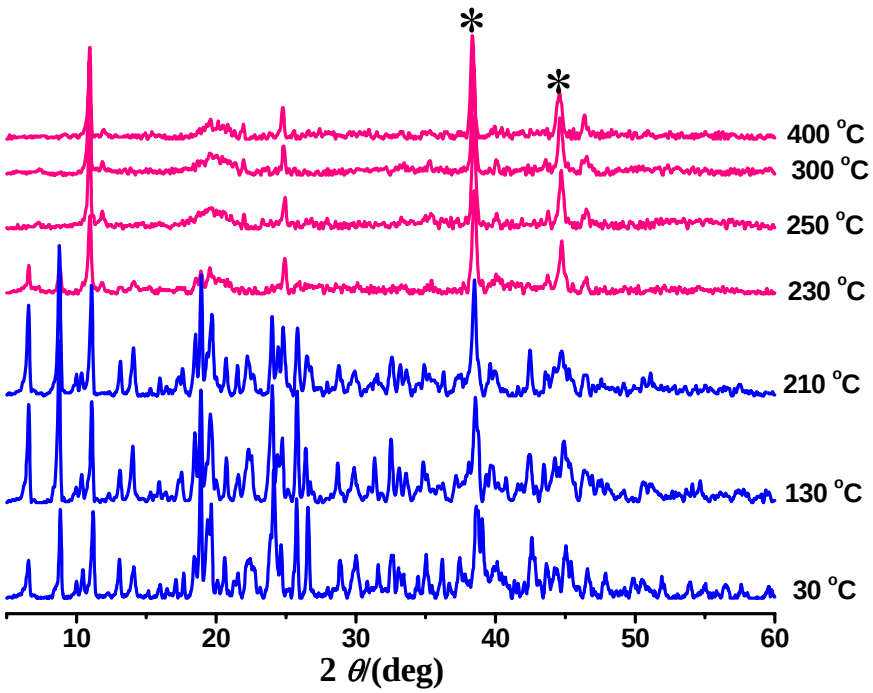


Fig S5 Variable-temperature X-ray powder diffraction (VTXRPD) of **1** under N_2 blowing at standard atmospheric pressure from 30 °C to 400 °C. (∗ marks the diffraction peak of back ground)

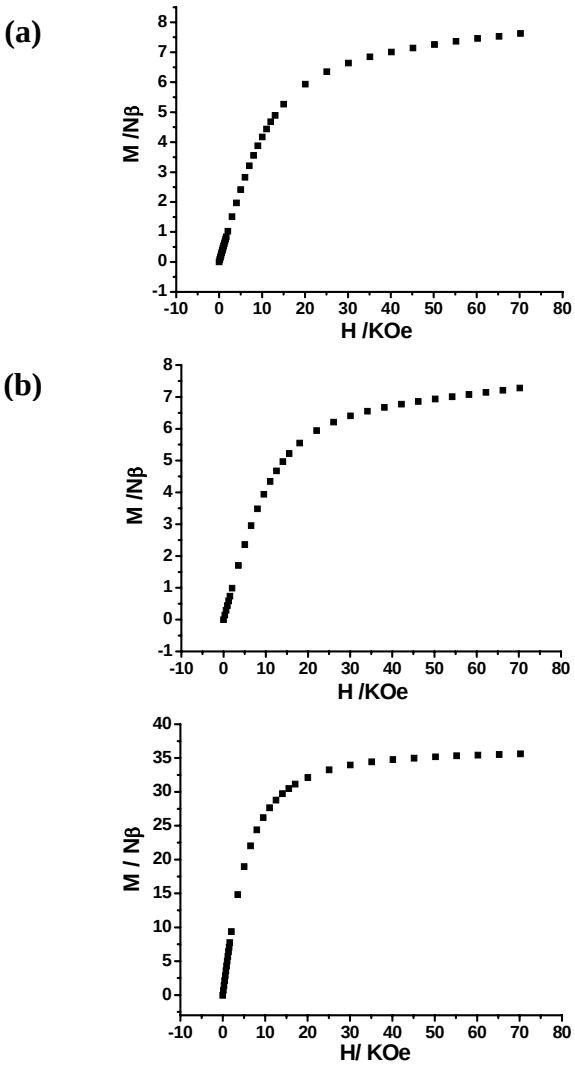
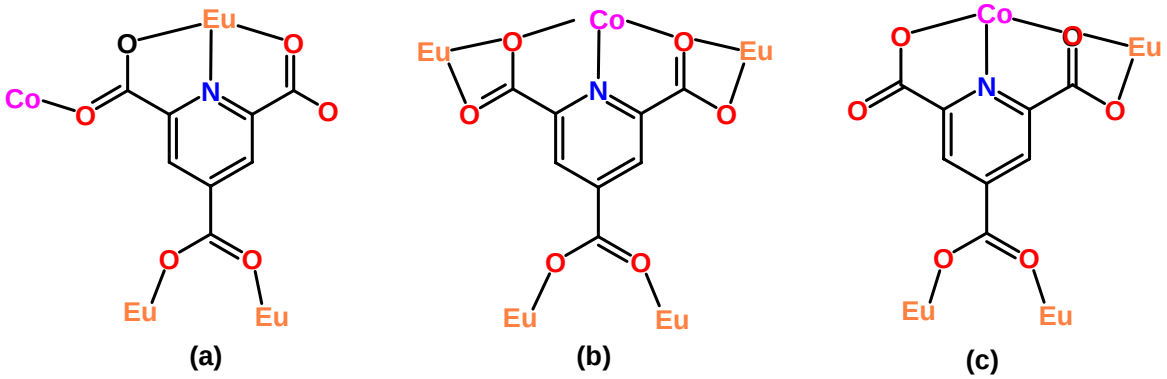


Fig S6 Plots of M-H at 2K for **1**(a), **2**(b) and **3**(c).



Scheme S1 Bridging modes of $pyta^{3-}$ ligand in **2.**

Table S1. Selected bond lengths (Å) and angles (°) for **2**.

	2		
Eu(1)-O(9a)	2.325(14)	Eu(2)-O(10d)	2.286(13)
Eu(1)-O(4b)	2.383(14)	Eu(2)-O(10e)	2.286(13)
Eu(1)-O(18)	2.391(14)	Eu(2)-O(15d)	2.437(13)
Eu(1)-O(13)	2.431(16)	Eu(2)-O(15e)	2.437(13)
Eu(1)-O(16c)	2.440(13)	Eu(2)-O(5)	2.499(13)
Eu(1)-O(1w)	2.491(17)	Eu(2)-O(5f)	2.499(13)
Eu(1)-O(1)	2.560(13)	Eu(2)-O(6)	2.544(12)
Eu(1)-N(3)	2.573(15)	Eu(2)-O(6f)	2.544(12)
Eu(1)-O(2)	2.654(14)	Co(1)-N(1)	2.003(14)
Eu(3)-O(3b)	2.307(15)	Co(1)-N(2)	2.006(15)
Eu(3)-O(3g)	2.307(15)	Co(1)-O(12)	2.102(14)
Eu(3)-O(2w)	2.426(17)	Co(1)-O(1)	2.106(13)
Eu(3)-O(2wf)	2.426(17)	Co(1)-O(7)	2.167(14)
Eu(3)-O(7)	2.495(13)	Co(1)-O(6)	2.192(12)
Eu(3)-O(7f)	2.495(13)	Co(2)-O(4w)	1.98(4)
Eu(3)-O(8)	2.575(13)	Co(2)-O(4wh)	1.98(4)
Eu(3)-O(8f)	2.575(13)	Co(2)-O(5wh)	2.11(3)
Eu(3)-O(3w)	2.59(5)	Co(2)-O(5w)	2.11(3)
Co(2)-O(6wh)	2.21(4)	Co(2)-O(14h)	2.113(14)
Co(2)-O(6w)	2.21(4)	Co(2)-O(14)	2.113(14)
Co(2)-O(7wh)	2.13(5)	Co(2)-O(7w)	2.13(5)
O(9a)-Eu(1)-O(4b)	85.6(6)	O(16c)-Eu(1)-O(1)	149.4(5)
O(9a)-Eu(1)-O(18)	149.9(5)	O(1w)-Eu(1)-O(1)	138.1(5)
O(4b)-Eu(1)-O(18)	82.1(5)	O(9a)-Eu(1)-N(3)	138.5(6)
O(9a)-Eu(1)-O(13)	79.5(6)	O(4b)-Eu(1)-N(3)	134.6(5)
O(4b)-Eu(1)-O(13)	142.9(5)	O(18)-Eu(1)-N(3)	63.3(5)
O(18)-Eu(1)-O(13)	125.2(5)	O(13)-Eu(1)-N(3)	62.0(5)

O(9a)-Eu(1)-O(16c)	77.9(5)	O(16c)-Eu(1)-N(3)	78.0(5)
O(4b)-Eu(1)-O(16c)	134.3(5)	O(1w)-Eu(1)-N(3)	122.5(5)
O(18)-Eu(1)-O(16c)	91.3(5)	O(1)-Eu(1)-N(3)	73.0(4)
O(13)-Eu(1)-O(16c)	75.2(5)	O(9a)-Eu(1)-O(2)	68.9(5)
O(9a)-Eu(1)-O(1w)	77.1(6)	O(4b)-Eu(1)-O(2)	70.2(5)
O(4b)-Eu(1)-O(1w)	67.4(5)	O(18)-Eu(1)-O(2)	130.6(5)
O(18)-Eu(1)-O(1w)	72.9(5)	O(13)-Eu(1)-O(2)	72.8(5)
O(13)-Eu(1)-O(1w)	139.1(5)	O(16c)-Eu(1)-O(2)	137.2(5)
O(16c)-Eu(1)-O(1w)	67.4(5)	O(1w)-Eu(1)-O(2)	126.8(5)
O(9a)-Eu(1)-O(1)	118.8(5)	O(1)-Eu(1)-O(2)	49.9(4)
O(4b)-Eu(1)-O(1)	75.2(5)	N(3)-Eu(1)-O(2)	110.0(5)
O(18)-Eu(1)-O(1)	84.3(5)	O(10d)-Eu(2)-O(10e)	158.1(7)
O(13)-Eu(1)-O(1)	82.7(5)	O(10d)-Eu(2)-O(15d)	80.4(5)
O(15d)-Eu(2)-O(5)	155.5(5)	O(10e)-Eu(2)-O(15d)	83.7(5)
O(15e)-Eu(2)-O(5)	75.1(5)	O(10d)-Eu(2)-O(15e)	83.7(5)
O(10d)-Eu(2)-O(5f)	77.0(4)	O(10e)-Eu(2)-O(15e)	80.4(5)
O(10e)-Eu(2)-O(5f)	113.3(5)	O(15d)-Eu(2)-O(15e)	86.9(7)
O(15d)-Eu(2)-O(5f)	75.1(5)	O(10d)-Eu(2)-O(5)	113.3(5)
O(15e)-Eu(2)-O(5f)	155.5(5)	O(10e)-Eu(2)-O(5)	77.0(4)
O(5)-Eu(2)-O(5f)	126.6(7)	O(10d)-Eu(2)-O(6f)	123.1(4)
O(10d)-Eu(2)-O(6)	75.6(4)	O(10e)-Eu(2)-O(6f)	75.6(4)
O(10e)-Eu(2)-O(6)	123.1(4)	O(15d)-Eu(2)-O(6f)	104.8(5)
O(15d)-Eu(2)-O(6)	151.8(4)	O(15e)-Eu(2)-O(6f)	151.8(4)
O(15e)-Eu(2)-O(6)	104.8(5)	O(5)-Eu(2)-O(6f)	85.1(5)
O(5)-Eu(2)-O(6)	51.8(4)	O(5f)-Eu(2)-O(6f)	51.8(4)
O(5f)-Eu(2)-O(6)	85.1(5)	O(6)-Eu(2)-O(6f)	77.0(6)
O(3g)-Eu(3)-O(7)	125.2(5)	O(3b)-Eu(3)-O(3g)	150.5(9)
O(2w)-Eu(3)-O(7)	142.3(6)	O(3b)-Eu(3)-O(2w)	84.5(7)
O(2wf)-Eu(3)-O(7)	79.8(6)	O(3g)-Eu(3)-O(2w)	83.6(7)
O(3b)-Eu(3)-O(7f)	125.2(5)	O(3b)-Eu(3)-O(2wf)	83.6(7)

O(3g)-Eu(3)-O(7f)	78.8(6)	O(3g)-Eu(3)-O(2wf)	84.5(7)
O(2w)-Eu(3)-O(7f)	79.8(6)	O(2w)-Eu(3)-O(2wf)	131.7(10)
O(2wf)-Eu(3)-O(7f)	142.3(6)	O(3b)-Eu(3)-O(7)	78.8(6)
O(7)-Eu(3)-O(7f)	82.8(7)	O(2w)-Eu(3)-O(8f)	69.5(6)
O(3b)-Eu(3)-O(8)	126.1(5)	O(2wf)-Eu(3)-O(8f)	147.5(6)
O(3g)-Eu(3)-O(8)	73.6(5)	O(7)-Eu(3)-O(8f)	73.4(5)
O(2w)-Eu(3)-O(8)	147.5(6)	O(7f)-Eu(3)-O(8f)	51.7(4)
O(2wf)-Eu(3)-O(8)	69.5(6)	O(8)-Eu(3)-O(8f)	105.8(7)
O(7)-Eu(3)-O(8)	51.7(4)	O(3b)-Eu(3)-O(3w)	75.3(4)
O(7f)-Eu(3)-O(8)	73.4(5)	O(3g)-Eu(3)-O(3w)	75.3(4)
O(3b)-Eu(3)-O(8f)	73.6(5)	O(2w)-Eu(3)-O(3w)	65.8(5)
O(3g)-Eu(3)-O(8f)	126.1(5)	O(2wf)-Eu(3)-O(3w)	65.9(5)
N(1)-Co(1)-N(2)	165.5(6)	O(7)-Eu(3)-O(3w)	138.6(3)
N(1)-Co(1)-O(12)	103.1(6)	O(7f)-Eu(3)-O(3w)	138.6(3)
N(2)-Co(1)-O(12)	77.0(6)	O(8)-Eu(3)-O(3w)	127.1(3)
N(1)-Co(1)-O(1)	77.2(5)	O(8f)-Eu(3)-O(3w)	127.1(3)
N(2)-Co(1)-O(1)	117.3(6)	O(4wh)-Co(2)-O(5wh)	90.3(15)
O(12)-Co(1)-O(1)	90.6(6)	O(4w)-Co(2)-O(5w)	90.3(15)
N(1)-Co(1)-O(7)	104.5(6)	O(4wh)-Co(2)-O(5w)	124.8(15)
N(2)-Co(1)-O(7)	77.1(6)	O(5wh)-Co(2)-O(5w)	34.5(18)
O(12)-Co(1)-O(7)	152.3(5)	O(4w)-Co(2)-O(14h)	90.0(12)
O(1)-Co(1)-O(7)	92.5(6)	O(4wh)-Co(2)-O(14h)	89.7(12)
N(1)-Co(1)-O(6)	76.1(5)	O(5wh)-Co(2)-O(14h)	90.7(10)
N(2)-Co(1)-O(6)	89.5(5)	O(5w)-Co(2)-O(14h)	90.4(10)
O(12)-Co(1)-O(6)	97.7(6)	O(4w)-Co(2)-O(14)	89.7(12)
O(1)-Co(1)-O(6)	153.1(5)	O(4wh)-Co(2)-O(14)	90.0(12)
O(7)-Co(1)-O(6)	91.9(5)	O(5wh)-Co(2)-O(14)	90.4(10)
O(4w)-Co(2)-O(4wh)	145(2)	O(5w)-Co(2)-O(14)	90.7(10)
O(4w)-Co(2)-O(5wh)	124.8(15)	O(14h)-Co(2)-O(14)	178.8(9)
O(4w)-Co(2)-O(7w)	102.9(19)	O(4wh)-Co(2)-O(6wh)	174.8(17)

O(4wh)-Co(2)-O(7w)	42.0(17)	O(5wh)-Co(2)-O(6wh)	85.3(14)
O(5wh)-Co(2)-O(7w)	132.2(16)	O(5w)-Co(2)-O(6wh)	50.8(14)
O(5w)-Co(2)-O(7w)	166.6(16)	O(14h)-Co(2)-O(6wh)	93.1(11)
O(14h)-Co(2)-O(7w)	91.8(14)	O(14)-Co(2)-O(6wh)	87.4(11)
O(14)-Co(2)-O(7w)	87.2(14)	O(7w)-Co(2)-O(6wh)	142.1(17)
O(4w)-Co(2)-O(7wh)	42.0(17)	O(7wh)-Co(2)-O(6wh)	81.7(17)
O(4wh)-Co(2)-O(7wh)	103(2)	O(4w)-Co(2)-O(6w)	174.8(17)
O(5wh)-Co(2)-O(7wh)	166.6(16)	O(4wh)-Co(2)-O(6w)	39.6(15)
O(5w)-Co(2)-O(7wh)	132.2(16)	O(5wh)-Co(2)-O(6w)	50.8(14)
O(14h)-Co(2)-O(7wh)	87.2(14)	O(5w)-Co(2)-O(6w)	85.3(14)
O(14)-Co(2)-O(7wh)	91.8(14)	O(14h)-Co(2)-O(6w)	87.4(11)
O(7w)-Co(2)-O(7wh)	61(3)	O(14)-Co(2)-O(6w)	93.1(11)
O(4w)-Co(2)-O(6wh)	39.6(15)	O(7w)-Co(2)-O(6w)	81.7(17)
O(6wh)-Co(2)-O(6w)	136(2)	O(7wh)-Co(2)-O(6w)	142.1(18)

Symmetry codes for **2:** *a*) x+1/2, -y+3/2, z+1/2; *b*) -x-1/2, -y+3/2, -z; *c*) -x-1/2, -y+3/2, -z-1; *d*) x, -y+1, z+1/2; *e*) -x-1, -y+1, -z-1; *f*) -x-1, y, -z-1/2; *g*) x-1/2, -y+3/2, z-1/2; *h*) -x, y, -z-1/2.