

**{[Cu<sub>3</sub>Lu<sub>2</sub>(ODA)<sub>6</sub>(H<sub>2</sub>O)<sub>6</sub>]•10H<sub>2</sub>O}<sub>n</sub> . First heterometallic framework  
based on copper(II)/lutetium(III) for the catalytic oxidation of  
olefins and aromatic benzylic substrates .**

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## Supplementary Material

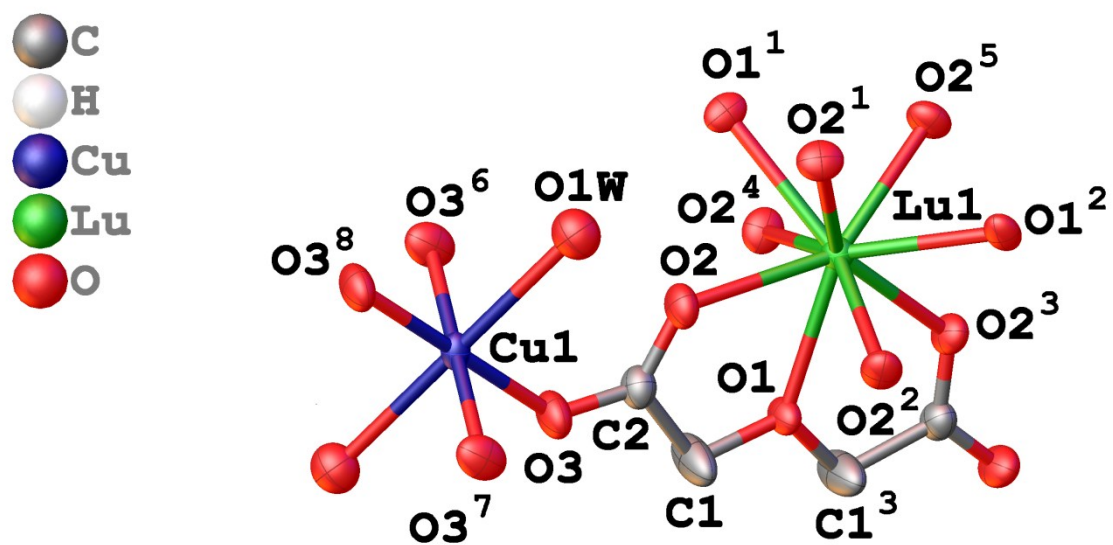
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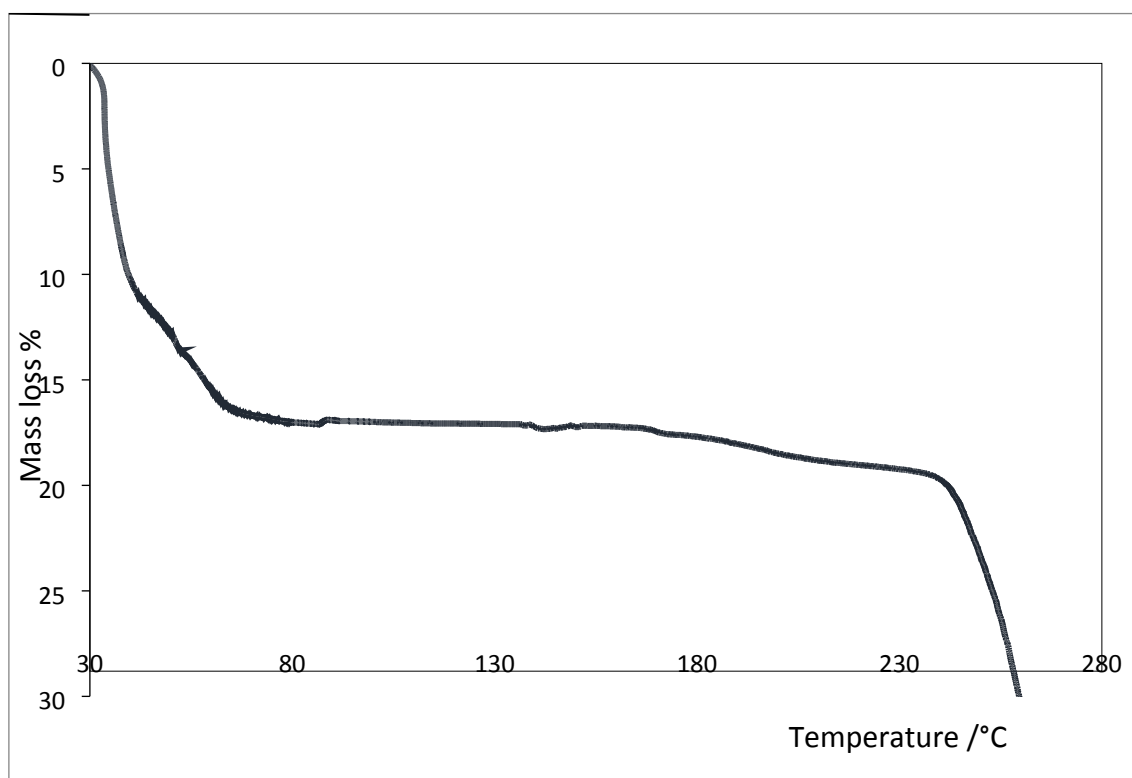
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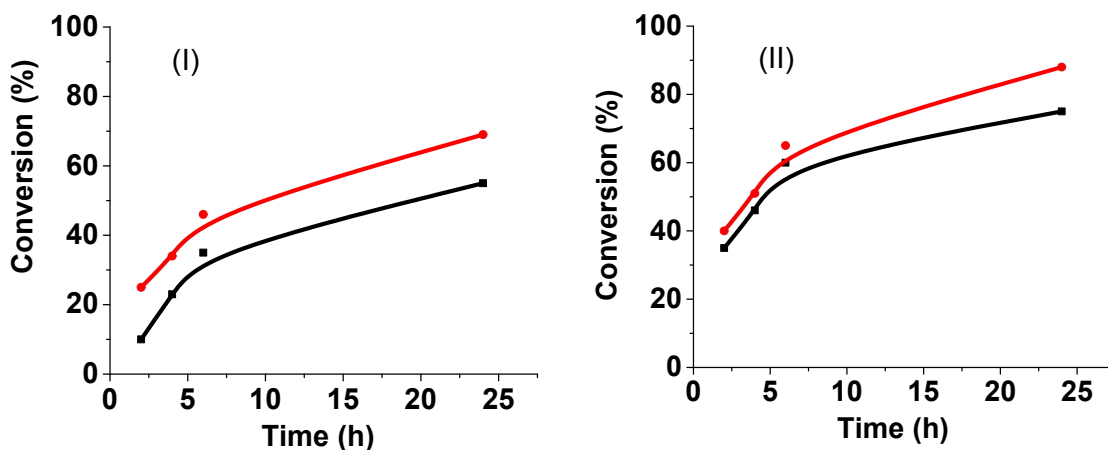
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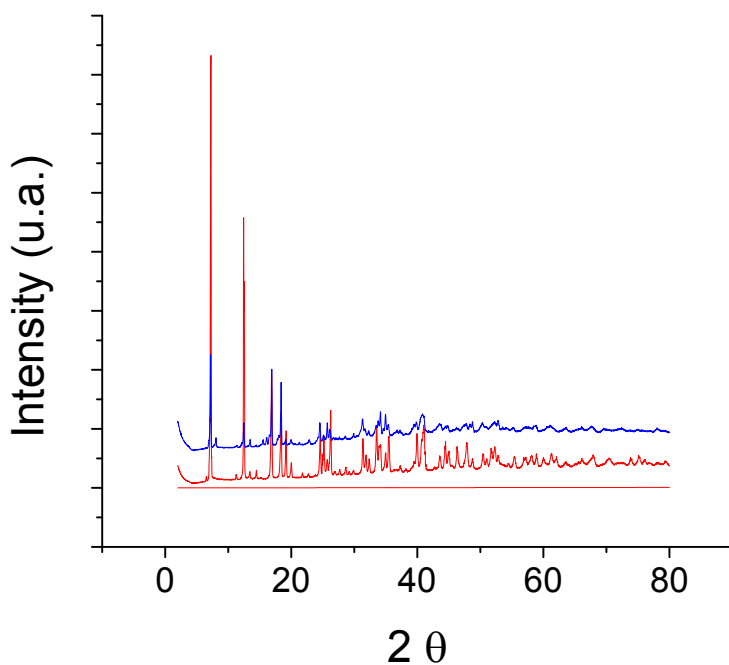
**Figure 1S.** ORTEP view and labeling scheme for  $[\text{Cu}_3\text{Lu}_2(\text{ODA})_6(\text{H}_2\text{O})_6]$ .



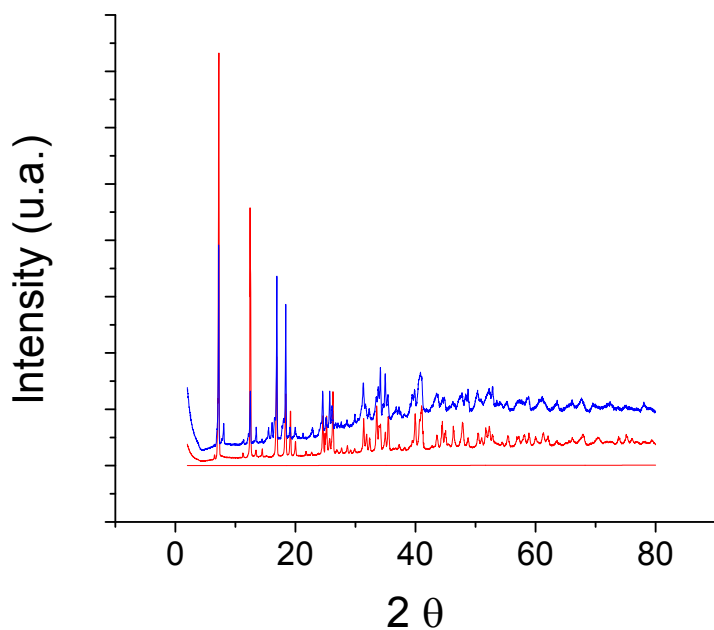
**Figure 2S.** Thermogravimetric analysis of  $\{[\text{Cu}_3\text{Lu}_2(\text{ODA})_6(\text{H}_2\text{O})_6] \cdot 10\text{H}_2\text{O}\}_n$ .



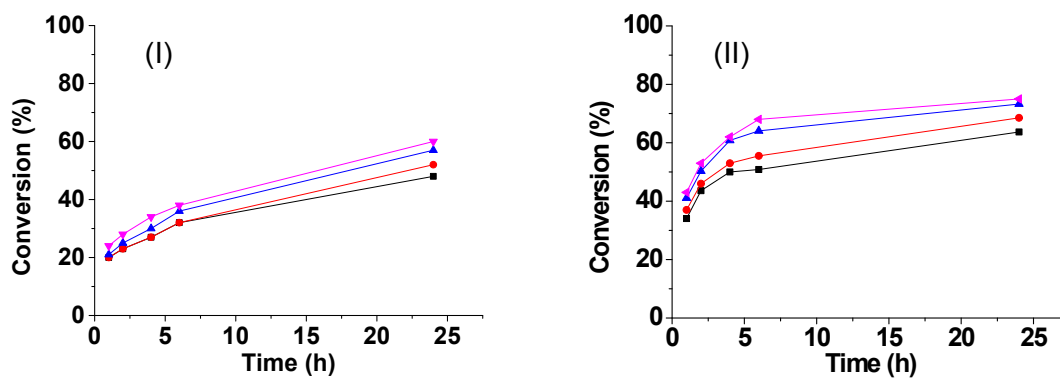
**Figure 3S.** Temporal evolution of (I) the conversion of cyclohexene. (II) the conversion of styrene. Black line: using DCE as solvent; Red line: using n-decane as solvent. Reaction conditions: TBHP (70% in water) or 5,5M in n-decane as oxidant, 75°C, 24h of reaction and ratio S/C = 2400/1 or 0.001mol% of copper per mole of substrate.



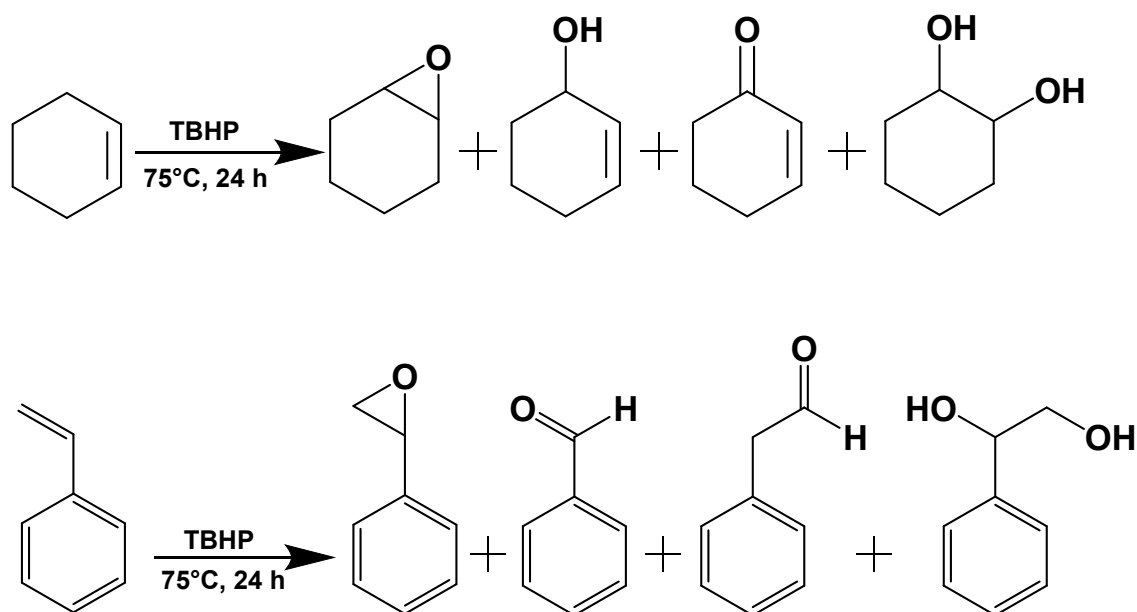
**Figure 4S.** Diffractogram of CuLuMOF before the catalytic oxidation of styrene (red line) and after the catalytic oxidation of styrene (blue line).



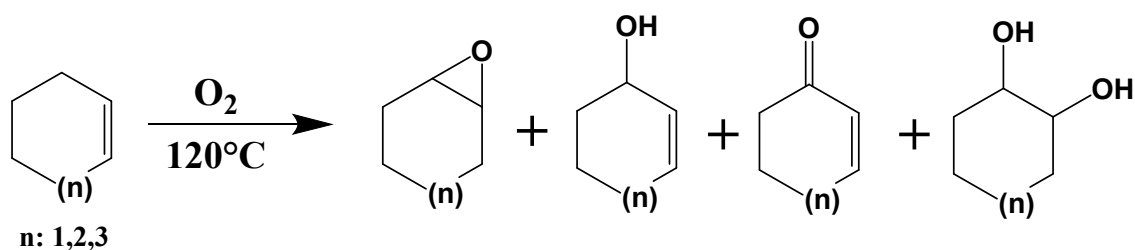
**Figure 5S.** Diffractogram of CuLuMOF before the catalytic oxidation of cyclohexene (red line) and after the catalytic oxidation of cyclohexene (blue line).



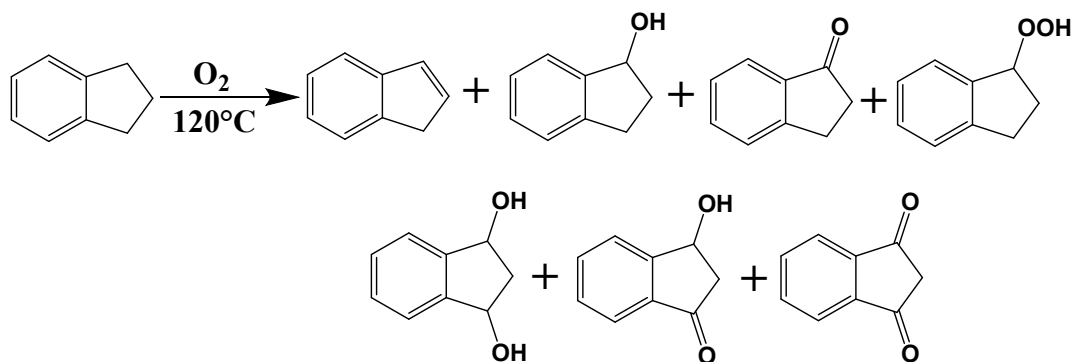
**Figure 6S.** (I) Temporal evolution of the conversion of cyclohexene. (II) Temporal evolution of the conversion of styrene. Black line: CuLaMOF [1]; Red line: CuGdMOF [1]; Blue line: CuYbMOF [1]; Pink line: CuLuMOF [this work]. Reaction conditions: 1,2-dichloroethane as solvent, TBHP (70% in water) as oxidant, 75°C, 24h of reaction and ratio S/C = 2400/1 or 0.001mol% of copper per mole of substrate.



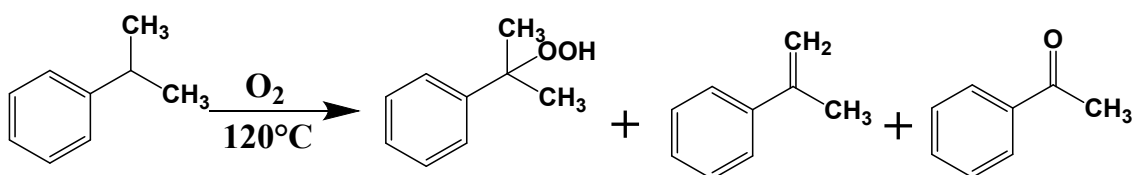
**Scheme 1S.** Scheme of the obtained products derived from the catalytic oxidation of cyclohexene and styrene (solvents 1,2-DCE or n-decane).



**Scheme 2S.** Scheme of the obtained products derived from the catalytic oxidation of cycloalkenes (cyclohexene (C6), cycloheptene (C7) and cyclooctene (C8)) (solventless medium).



**Scheme 3S.** Scheme of the obtained products derived from the catalytic oxidation of indan.(solventless medium)



**Scheme 4S.** Scheme of the obtained products derived from the catalytic oxidation of cumene (solventless medium).

### Synthesis and Characterization of [Cu<sub>3</sub>Lu<sub>2</sub>(ODA)<sub>6</sub>(H<sub>2</sub>O)<sub>6</sub>].10H<sub>2</sub>O (CuLuMOF)

LuCl<sub>3</sub>·6H<sub>2</sub>O (0.193 g, 0.50 mmol) and CuCl<sub>2</sub>·6H<sub>2</sub>O (0.127 g, 0.52 mmol) were dissolved in 5 mL of water. 2,2-oxidiacetic acid (0.20 g, 1.5 mmol) was dissolved in another 5 mL of water, and the pH value was adjusted to 6.5 with ammonium hydroxide. Both solutions were mixed, and a clear solution was obtained. The solution was allowed to evaporate slowly at room temperature. After two days, light blue crystals were obtained. Yield 50-70%. Anal. Calc. for C<sub>24</sub>H<sub>56</sub>O<sub>46</sub>Cu<sub>3</sub>Lu<sub>2</sub>: C, 17.8; H, 3.5. Found: C, 17.5; H, 3.8 %.

### Thermogravimetric analysis

Thermal analysis was performed on a Shimadzu TGA-50 instrument with a TA 50 I interface, using a platinum cell and nitrogen atmosphere. Experimental conditions were 0.5 °C min<sup>-1</sup> temperature ramp rate and 5 mL min<sup>-1</sup> nitrogen flow rate.

Quantification of the water content by thermogravimetric analysis showed that the sixteen water molecules were lost across a wide temperature range, between 30 and 90 °C. This is consistent with the presence of a set of weakly bonded water molecules. No clear steps could be distinguished in the TGA diagram. The experimental mass loss (17.1%) is in agreement with the corresponding value for 16 water molecules (17.7%). Decomposition of the MOF is evident from 240 °C.

### Elemental analysis

Elemental analysis (C, H) was performed on a Thermo Scientific FLASH 2000 instrument.

### X-ray data collection and refinement.

A summary of crystal data, data collection, structure determination and refinement for  $[\text{Cu}_3\text{Lu}_2(\text{ODA})_6(\text{H}_2\text{O})_6]$  is given in **Table 1SA**.

Diffraction data were collected at room temperature using a Bruker D8 Venture single crystal diffractometer equipped with a MoK $\alpha$  sealed tube X-ray source operating at 50 kV/30 mA and a PHOTON 100 area detector operating in shutterless mode. Unit cell determination, data collection and processing were performed using the Bruker APEX3 software suite [2]. Structure determination and refinement were performed with SHELXT and SHELXL (with OLEX2 graphical user interface) programs respectively [3-5]. A maximum number of 10 crystallization water molecules per formula unit was established by TGA and EA in single-crystal samples. They could not be refined adequately because of being highly disordered. To avoid this problem a solvent masking procedure was applied to disordered electron density in the cavities using the OLEX2 program [4]. Hydrogen atoms on O1W and C2 were located geometrically and refined allowing to ride on their parent atoms with Uiso(H) = 1.5Ueq(O) and Uiso(H) = 1.2Ueq(C) respectively. Supplementary crystallographic information, bond lengths, bond angles and torsion angles can be found in tables 1SA, 1SB, 1SC and 1SE respectively. Crystallographic data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/structures](http://www.ccdc.cam.ac.uk/structures), CCDC 1532010.

**Table 1SA.** Crystal data, data collection, structure determination and refinement for  $[\text{Cu}_3\text{Lu}_2(\text{ODA})_6(\text{H}_2\text{O})_6]$ .

Empirical formula	$\text{C}_{24}\text{H}_{30}\text{Cu}_3\text{Lu}_2\text{O}_{36}$
Formula weight	1435.05
Temperature/K	293(2)
Crystal system	hexagonal
Space group	P6/mcc
a/Å	14.021(2)
b/Å	14.021(2)
c/Å	15.713(2)
$\alpha/^\circ$	90
$\beta/^\circ$	90
$\gamma/^\circ$	120
Volume/Å <sup>3</sup>	2675.1(9)
Z	2
$\rho_{\text{calc}}/\text{g}/\text{cm}^3$	1.782
$\mu/\text{mm}^{-1}$	4.920
F(000)	1382.0
Crystal size/mm <sup>3</sup>	0.256 × 0.090 × 0.061
Radiation	Mo Ka ( $\lambda = 0.71073$ )
2 $\theta$ range for data collection/ $^\circ$	5.82 to 61.02
Index ranges	-19 ≤ h ≤ 20 -20 ≤ k ≤ 20 -22 ≤ l ≤ 22
Reflections collected	81028
Independent reflections	1417 [ $R_{\text{int}} = 0.0743$ , $R_{\text{sigma}} = 0.0150$ ]
Data/restraints/parameters	1417/0/56

Goodness-of-fit on $F^2$	1.132
Final R indexes [ $I \geq 2s(I)$ ]	R1 = 0.0224, wR2 = 0.0473
Final R indexes [all data]	R1 = 0.0394, wR2 = 0.0590
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	0.56/-0.77

**Table 1SB.** Crystallographic information for  $[\text{Cu}_3\text{Lu}_2(\text{ODA})_6(\text{H}_2\text{O})_6]$ . Fractional atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ).  $U_{eq}$  is defined as 1/3 of the trace of the orthogonalised  $U_{ij}$  tensor.

Atom	x	y	z	U(eq)
Lu1	6667	3333	7500	20.38(8)
Cu1	5000	5000	5000	20.47(14)
O1	7661.3(12)	5323(2)	7500	27.5(6)
O1W	4868(4)	3185(3)	5000	45.4(10)
O2	6095(2)	4149(2)	6476.0(14)	31.6(5)
O3	6158(2)	5624(2)	5862.1(17)	38.4(6)
C1	7441(4)	5940(3)	6915(3)	56.2(13)
C2	6481(3)	5176(3)	6381(2)	29.6(7)

**Table 1SC.** Selected bond lengths for  $[\text{Cu}_3\text{Lu}_2(\text{ODA})_6(\text{H}_2\text{O})_6]$ .

Atom	Atom	Length/ $\text{\AA}$
Lu1	O1	2.415(3)
Lu1	O2	2.336(2)
Cu1	O1W	2.457(4)
Cu1	O3	1.953(3)
O1	C1	1.398(4)
O2	C2	1.268(4)
O3	C2	1.246(4)
C1	C2	1.491(5)

**Table 1SD.** Selected bond angles for  $[\text{Cu}_3\text{Lu}_2(\text{ODA})_6(\text{H}_2\text{O})_6]$ .

Atom	Atom	Atom	Angle/ $^\circ$
O1 <sup>2</sup>	Lu1	O1	120.0000(10)
O1 <sup>2</sup>	Lu1	O1 <sup>1</sup>	120.0
O1 <sup>1</sup>	Lu1	O1	120.0
O2 <sup>4</sup>	Lu1	O1 <sup>1</sup>	64.91(6)
O2 <sup>2</sup>	Lu1	O1	72.71(6)
O2 <sup>2</sup>	Lu1	O1 <sup>2</sup>	64.91(6)
O2 <sup>4</sup>	Lu1	O1	72.71(6)
O2 <sup>3</sup>	Lu1	O1 <sup>2</sup>	72.71(6)
O2 <sup>5</sup>	Lu1	O1 <sup>2</sup>	64.91(6)
O2 <sup>4</sup>	Lu1	O1 <sup>2</sup>	136.16(6)



O2	Lu1	O1 <sup>1</sup>	72.71(6)
O2 <sup>1</sup>	Lu1	O1 <sup>2</sup>	72.71(6)
O2 <sup>5</sup>	Lu1	O1	136.16(6)
O2 <sup>5</sup>	Lu1	O1 <sup>1</sup>	72.71(6)
O2 <sup>1</sup>	Lu1	O1	136.16(6)
O2 <sup>2</sup>	Lu1	O1 <sup>1</sup>	136.16(6)
O2	Lu1	O1	64.91(6)
O2 <sup>3</sup>	Lu1	O1 <sup>1</sup>	136.16(6)
O2	Lu1	O1 <sup>2</sup>	136.16(6)
O2 <sup>1</sup>	Lu1	O1 <sup>1</sup>	64.91(6)
O2 <sup>3</sup>	Lu1	O1	64.91(6)
O2 <sup>5</sup>	Lu1	O2 <sup>4</sup>	77.78(9)
O2 <sup>4</sup>	Lu1	O2	87.68(11)
O2 <sup>2</sup>	Lu1	O2 <sup>1</sup>	77.78(9)
O2 <sup>2</sup>	Lu1	O2 <sup>4</sup>	145.42(13)
O2 <sup>5</sup>	Lu1	O2 <sup>3</sup>	77.78(9)
O2 <sup>3</sup>	Lu1	O2 <sup>4</sup>	77.78(9)
O2 <sup>1</sup>	Lu1	O2	77.78(9)

<sup>1</sup>1-Y,+X-Y,+Z; <sup>2</sup>1+Y-X,1-X,+Z; <sup>3</sup>1+Y-X,+Y,3/2-Z; <sup>4</sup>1-Y,1-X,3/2-Z; <sup>5</sup>+X,+X-Y,3/2-Z; <sup>6</sup>1-X,1-Y,+Z; <sup>7</sup>+X,+Y,1-Z; <sup>8</sup>1-X,1-Y,1-Z

**Table 1SE.** Selected torsion angles for [Cu<sub>3</sub>Lu<sub>2</sub>(ODA)<sub>6</sub>(H<sub>2</sub>O)<sub>6</sub>].

A	B	C	D	Angle/°
Lu1	O1	C1	C2	4.2(5)
Lu1	O2	C2	O3	-176.9(3)
Lu1	O2	C2	C1	5.3(5)
Cu1	O3	C2	O2	-1.0(6)
Cu1	O3	C2	C1	176.8(3)
O1	C1	C2	O2	-5.8(6)
O1	C1	C2	O3	176.2(3)
C1 <sup>1</sup>	O1	C1	C2	-175.8(5)

<sup>1</sup>1+Y-X,+Y,3/2-Z

## References

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5. Dolomanov, O.V., et al., *OLEX2: a complete structure solution, refinement and analysis program*. Journal of Applied Crystallography, 2009. **42**(2): p. 339-341.