Electronic Supplementary Material (ESI) for New Journal of Chemistry.


# Supplementary Material

## Influence of the channel size of isostructural 3d-4f MOFs on the catalytic aerobic oxidation of cycloalkenes.

P. Cancino[a,b], L. Santibañez[a], C. Stevens[a], P. Fuentealba[a,b], N. Audebrand[d], D. Aravena[e], J. Torres[c], S. Martinez[c], C. Kremer[c], E. Spodine*[a,b].

[a] *Facultad de Ciencias Químicas y Farmacéuticas, Universidad de Chile, Santiago, Chile*
[b] *Centro para el Desarrollo de la Nanociencia y la Nanotecnología, CEDENNA, Santiago, Chile*
[c] *Departamento Estrella Campos, Facultad de Química, Universidad de la República, Montevideo, Uruguay.*
[d] *Univ Rennes, CNRS, ISCR (Institut des Sciences Chimiques de Rennes) - UMR 6226, F-35000 Rennes, France.*
[e] *Departamento de Química y Biología, Universidad de Santiago de Chile, Santiago, Chile.*

*espodine@ciq.uchile.cl*

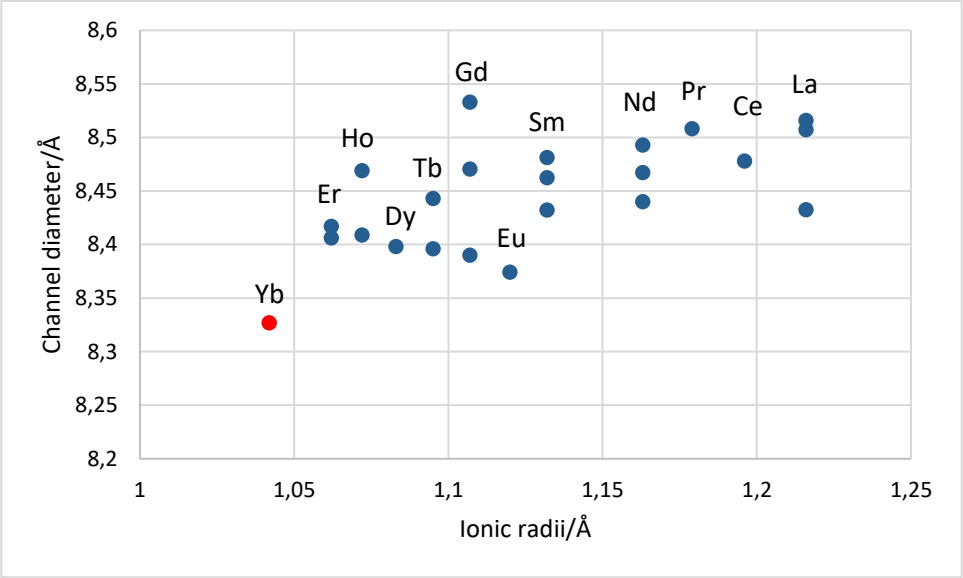



**Figure S1**. Variation of the channel diameter with ionic radii of lanthanide ions. Structural data were taken from previously reported values[1–9]. Red point represents the value for CuYbIDA. Shannon's radii for lanthanide(III) ions with coordination number 9 were used[10].

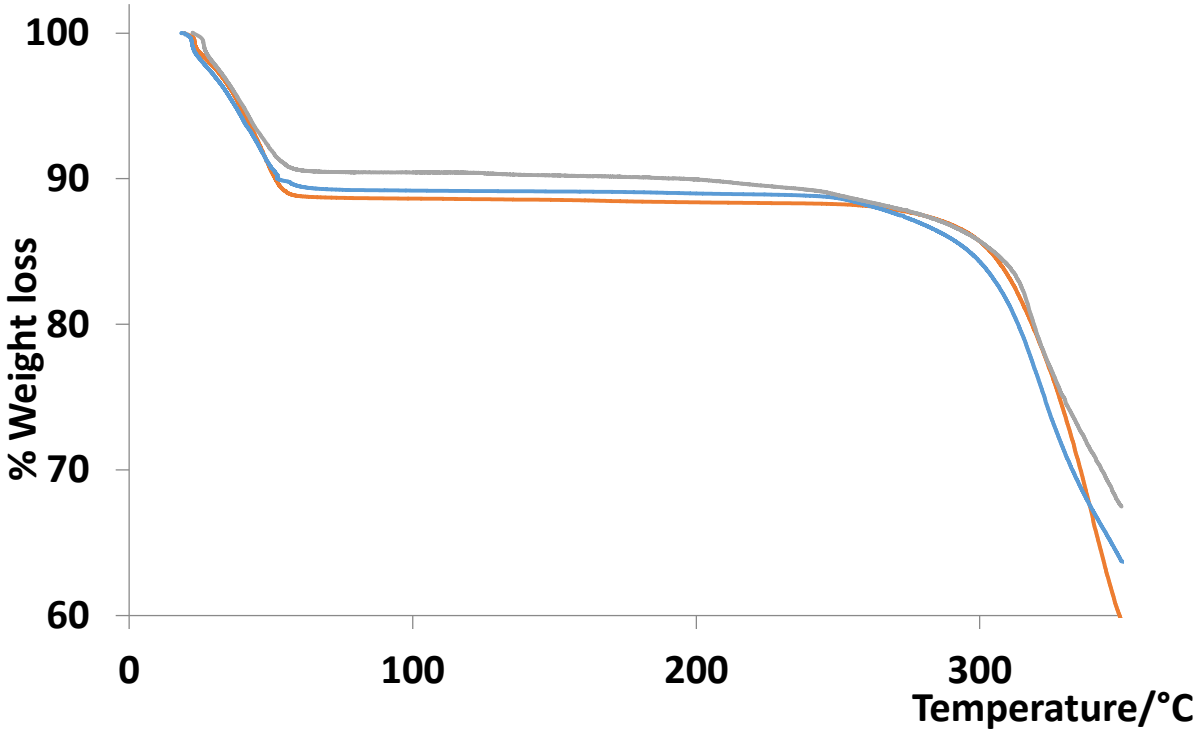
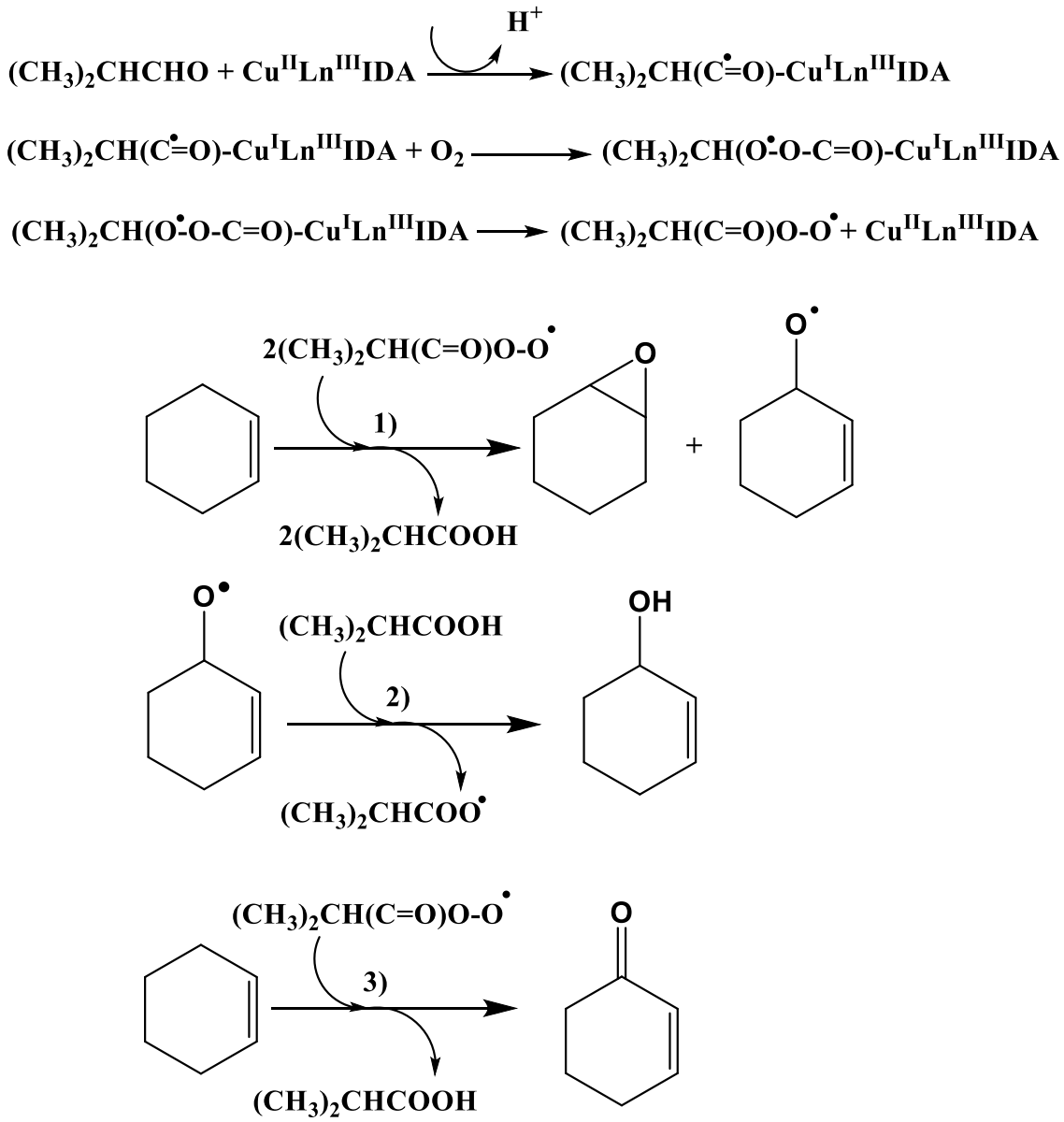



**Figure S2.** Thermogravimetric profiles of CuLaIDA (orange), CuGdIDA (green), CuYbIDA (blue).




**Scheme S1.** Proposed radical chain mechanism for the oxidation of cyclohexene[11,12].

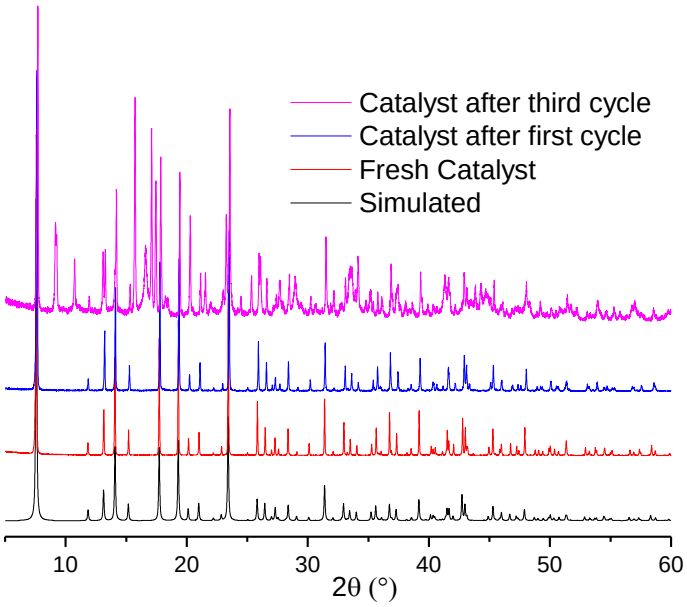



**Figure S3.** Powder X-ray diffractograms for CuLaIDA. Simulated (black), pristine ground crystals (red), after the first cycle (blue) and after the third cycle (pink).

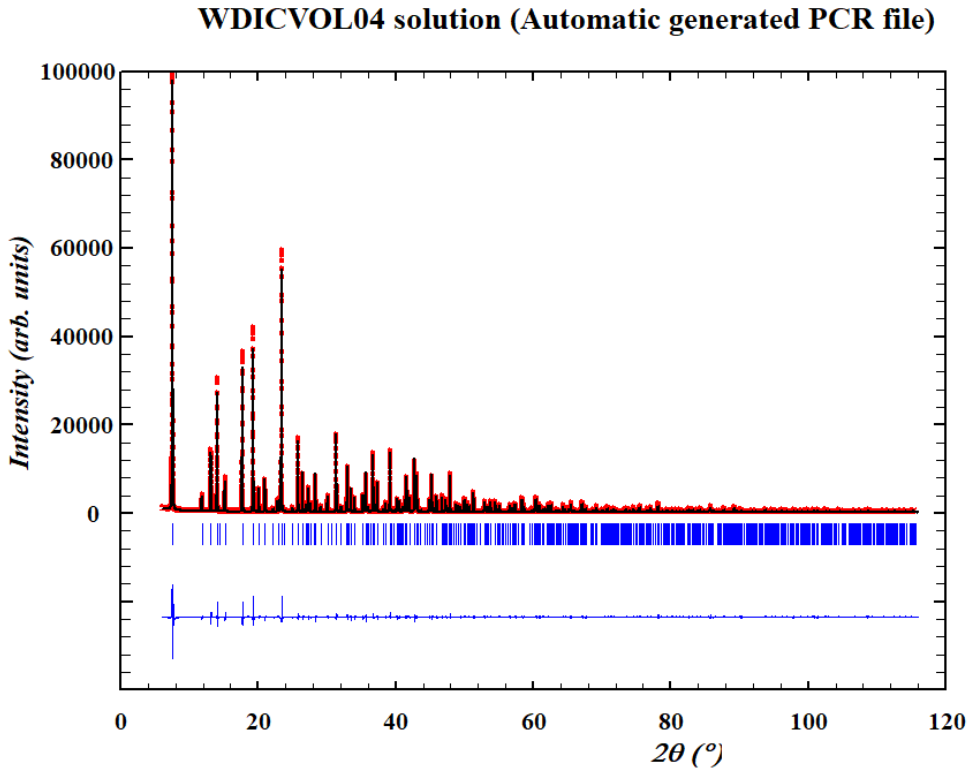



**Figure S4**. Le Bail fit of the powder pattern of the pristine ground crystals of CuLaIDA[13,14].

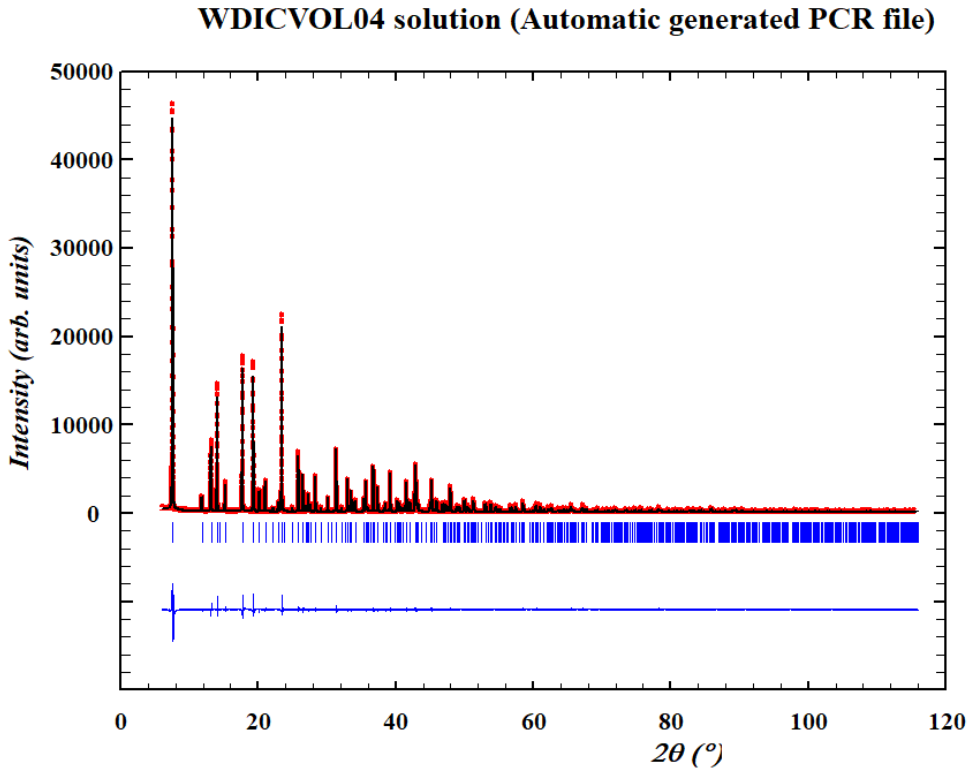



**Figure S5**. Le Bail fit of the powder pattern of the catalyst after the first cycle[13,14].

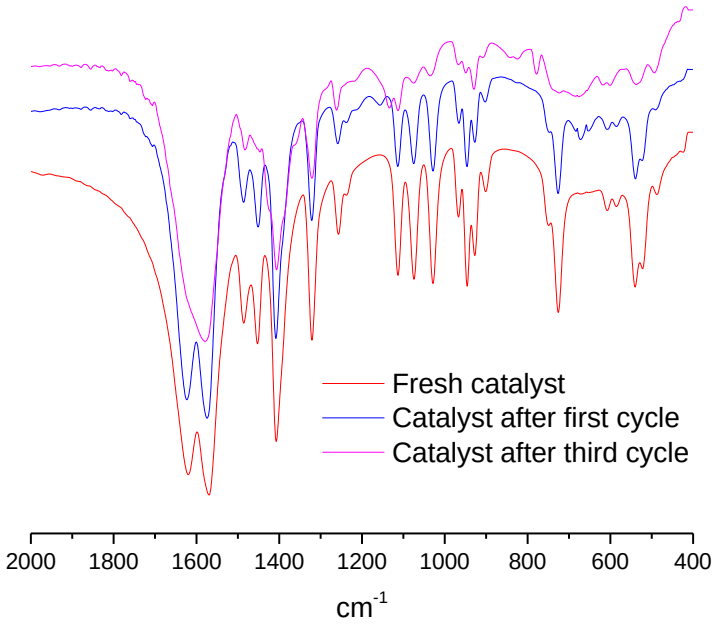



**Figure S6.** FTIR spectra for CuLaIDA. Pristine crystals (red), after the first cycle (blue) and after the third cycle (pink).

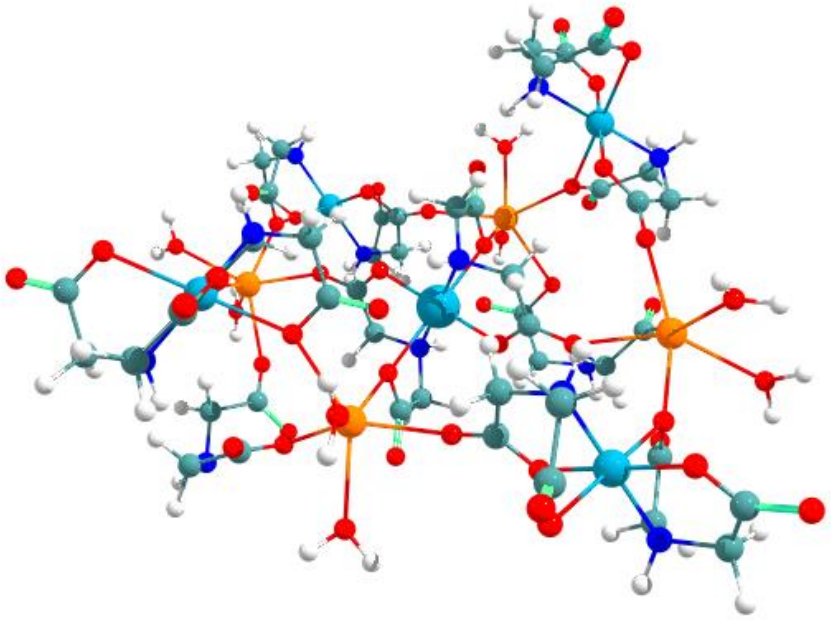


**Figure S8.** Model considered for electronic structure calculations. Color code: Ln (Dark orange), Cu/Zn (cyan), O (red), N (blue), C (gray), H (white).

**Table S1 Crystal data and structure refinement for CuYbIDA.**

| | |
|---|---|
| Identification code | CuYbIDA |
| Empirical formula | $C_{24}H_{30}Cu_3N_6O_{24}Yb_2$ |
| Formula weight (g/mol) | 1323.21 |
| Temperature/K | 100(2) |
| Crystal system | trigonal |
| Space group | *P*-3*c*1 |
| a/Å | 13.2638(3) |
| b/Å | 13.2638(3) |
| c/Å | 14.1414(3) |
| α/° | 90 |
| β/° | 90 |
| γ/° | 120 |
| Volume/Å$^3$ | 2154.56(11) |
| Z | 2 |
| $\rho_{calc}$g/cm$^3$ | 2.040 |
| μ/mm$^{-1}$ | 10.111 |
| F(000) | 1270.0 |
| Crystal size/mm$^3$ | 0.094 × 0.063 × 0.058 |
| Radiation | CuKα (λ = 1.54178) |
| 2Θ range for data collection/° | 7.696 to 133.178 |
| Index ranges | -15 ≤ h ≤ 15, -15 ≤ k ≤ 15, -15 ≤ l ≤ 16 |
| Reflections collected | 50552 |
| Independent reflections | 1278 [$R_{int}$ = 0.0954, $R_{sigma}$ = 0.0199] |
| Data/restraints/parameters | 1278/0/91 |
| Goodness-of-fit on F$^2$ | 1.085 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0239, $wR_2$ = 0.0495 |
| Final R indexes [all data] | $R_1$ = 0.0372, $wR_2$ = 0.0538 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.64/-0.48 |

$^a R_1=\Sigma||F_0|-|F_c||/\Sigma|F_c|$, $^b wR_2=\{\Sigma[w(F_0^2-F_c^2)2]/\Sigma[w(F_0^2)^2\}^{1/2}$

**Table S2 Fractional Atomic Coordinates (×10$^4$) and Equivalent Isotropic Displacement Parameters (Å$^2$×10$^3$) for YbCuIDA. $U_{eq}$ is defined as 1/3 of of the trace of the orthogonalised $U_{IJ}$ tensor.**

| Atom | *x* | *y* | *z* | U(eq) |
|---|---|---|---|---|
| Yb1 | 6666.67 | 3333.33 | 8340.3(2) | 8.96(11) |
| Cu1 | 5000 | 5000 | 5000 | 14.3(2) |
| O1 | 6220(2) | 4350(2) | 7324.4(19) | 20.4(7) |
| O2 | 5991(3) | 5257(2) | 6108(2) | 19.8(6) |
| O3 | 5503(3) | 3584(3) | 4420(2) | 21.2(7) |
| O4 | 4393(3) | 1919(3) | 3716(2) | 29.1(8) |
| N1 | 3890(3) | 3466(3) | 5599(2) | 12.3(7) |
| C1 | 4488(4) | 3295(4) | 6422(3) | 19.6(9) |
| C2 | 5640(4) | 4370(4) | 6630(2) | 13.2(7) |
| C3 | 3512(4) | 2524(3) | 4895(3) | 16.5(9) |
| C4 | 4532(4) | 2677(4) | 4302(3) | 17.2(9) |

**Table S3 Bond Lengths for CuYbIDA.**

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| Yb1 | O1[1] | 2.243(3) | Cu1 | N1 | 2.008(3) |
| Yb1 | O1[2] | 2.243(3) | Cu1 | O3 | 2.428(3) |
| Yb1 | O1 | 2.243(3) | Cu1 | O3[6] | 2.428(3) |
| Yb1 | O3[3] | 2.311(3) | O1 | C2 | 1.256(4) |
| Yb1 | O3[4] | 2.311(3) | O2 | C2 | 1.265(5) |
| Yb1 | O3[5] | 2.311(3) | O3 | C4 | 1.258(5) |
| Yb1 | O4[3] | 2.690(3) | O4 | C4 | 1.244(5) |
| Yb1 | O4[5] | 2.690(4) | N1 | C3 | 1.475(5) |
| Yb1 | O4[4] | 2.690(3) | N1 | C1 | 1.489(5) |
| Cu1 | O2 | 1.962(3) | C1 | C2 | 1.508(7) |
| Cu1 | O2[6] | 1.962(3) | C3 | C4 | 1.517(6) |
| Cu1 | N1[6] | 2.007(3) | | | |

[1]1+y-x,1-x,+z; [2]1-y,+x-y,+z; [3]1+y-x,+y,1/2+z; [4]+x,+x-y,1/2+z; [5]1-y,1-x,1/2+z; [6]1-x,1-y,1-z

**Table S4 Bond Angles for CuYbIDA.**

| Atom | Atom | Atom | Angle/˚ | Atom | Atom | Atom | Angle/˚ |
|---|---|---|---|---|---|---|---|
| O1[1] | Yb1 | O1[2] | 83.38(11) | O2 | Cu1 | O2[6] | 180.0 |
| O1[1] | Yb1 | O1 | 83.38(11) | O2 | Cu1 | N1[6] | 94.17(12) |
| O1[2] | Yb1 | O1 | 83.38(11) | O2[6] | Cu1 | N1[6] | 85.83(12) |
| O1[1] | Yb1 | O3[3] | 81.50(11) | O2 | Cu1 | N1 | 85.83(12) |
| O1[2] | Yb1 | O3[3] | 129.89(10) | O2[6] | Cu1 | N1 | 94.17(12) |
| O1 | Yb1 | O3[3] | 140.92(10) | N1[6] | Cu1 | N1 | 180.0 |
| O1[1] | Yb1 | O3[4] | 140.92(10) | O2 | Cu1 | O3 | 89.14(12) |
| O1[2] | Yb1 | O3[4] | 81.50(11) | O2[6] | Cu1 | O3 | 90.86(12) |
| O1 | Yb1 | O3[4] | 129.89(10) | N1[6] | Cu1 | O3 | 107.18(11) |
| O3[3] | Yb1 | O3[4] | 81.08(11) | N1 | Cu1 | O3 | 72.82(11) |
| O1[1] | Yb1 | O3[5] | 129.89(10) | O2 | Cu1 | O3[6] | 90.86(12) |
| O1[2] | Yb1 | O3[5] | 140.92(10) | O2[6] | Cu1 | O3[6] | 89.14(12) |
| O1 | Yb1 | O3[5] | 81.49(11) | N1[6] | Cu1 | O3[6] | 72.82(11) |
| O3[3] | Yb1 | O3[5] | 81.08(11) | N1 | Cu1 | O3[6] | 107.18(11) |
| O3[4] | Yb1 | O3[5] | 81.08(11) | O3 | Cu1 | O3[6] | 180.0 |
| O1[1] | Yb1 | O4[3] | 72.44(10) | C2 | O1 | Yb1 | 149.6(3) |
| O1[2] | Yb1 | O4[3] | 78.70(10) | C2 | O2 | Cu1 | 113.7(3) |
| O1 | Yb1 | O4[3] | 151.26(10) | C4 | O3 | Yb1[7] | 102.2(3) |
| O3[3] | Yb1 | O4[3] | 51.19(10) | C4 | O3 | Cu1 | 103.8(3) |
| O3[4] | Yb1 | O4[3] | 69.35(10) | Yb1[7] | O3 | Cu1 | 142.77(13) |
| O3[5] | Yb1 | O4[3] | 126.03(10) | C4 | O4 | Yb1[7] | 84.6(3) |
| O1[1] | Yb1 | O4[5] | 78.70(10) | C3 | N1 | C1 | 112.4(3) |
| O1[2] | Yb1 | O4[5] | 151.26(10) | C3 | N1 | Cu1 | 109.8(2) |
| O1 | Yb1 | O4[5] | 72.44(10) | C1 | N1 | Cu1 | 107.9(2) |
| O3[3] | Yb1 | O4[5] | 69.35(10) | N1 | C1 | C2 | 111.9(3) |
| O3[4] | Yb1 | O4[5] | 126.03(10) | O1 | C2 | O2 | 122.1(5) |
| O3[5] | Yb1 | O4[5] | 51.19(10) | O1 | C2 | C1 | 118.3(4) |
| O4[3] | Yb1 | O4[5] | 116.21(5) | O2 | C2 | C1 | 119.6(3) |
| O1[1] | Yb1 | O4[4] | 151.26(10) | N1 | C3 | C4 | 110.9(3) |
| O1[2] | Yb1 | O4[4] | 72.44(10) | O4 | C4 | O3 | 121.9(4) |
| O1 | Yb1 | O4[4] | 78.70(10) | O4 | C4 | C3 | 119.9(4) |
| O3[3] | Yb1 | O4[4] | 126.03(10) | O3 | C4 | C3 | 118.2(4) |
| O3[4] | Yb1 | O4[4] | 51.19(10) | O4 | C4 | Yb1[7] | 69.7(2) |
| O3[5] | Yb1 | O4[4] | 69.35(10) | O3 | C4 | Yb1[7] | 52.3(2) |
| O4[3] | Yb1 | O4[4] | 116.21(5) | C3 | C4 | Yb1[7] | 170.4(3) |
| O4[5] | Yb1 | O4[4] | 116.21(5) | | | | |

[1]1+y-x,1-x,+z; [2]1-y,+x-y,+z; [3]1+y-x,+y,1/2+z; [4]+x,+x-y,1/2+z; [5]1-y,1-x,1/2+z; [6]1-x,1-y,1-z; [7]1-y,1-x,-1/2+z

**Table S5 Hydrogen Bonds for CuYbIDA.**

| D | H | A | d(D-H)/Å | d(H-A)/Å | d(D-A)/Å | D-H-A/° |
|---|---|---|---|---|---|---|
| N1 | H1 | O4[1] | 1.00 | 1.97 | 2.879(4) | 150.1 |

[1]-y+x,+x,1-z

**Table S6 Torsion Angles for CuYbIDA.**

| A | B | C | D | Angle/° | A | B | C | D | Angle/° |
|---|---|---|---|---|---|---|---|---|---|
| C3 | N1 | C1 | C2 | 129.4(4) | Yb1[1] | O4 | C4 | O3 | -0.1(4) |
| Cu1 | N1 | C1 | C2 | 8.2(4) | Yb1[1] | O4 | C4 | C3 | 179.4(3) |
| Yb1 | O1 | C2 | O2 | -155.3(4) | Yb1[1] | O3 | C4 | O4 | 0.1(5) |
| Yb1 | O1 | C2 | C1 | 24.7(7) | Cu1 | O3 | C4 | O4 | 153.3(3) |
| Cu1 | O2 | C2 | O1 | 173.9(3) | Yb1[1] | O3 | C4 | C3 | -179.4(3) |
| Cu1 | O2 | C2 | C1 | -6.1(4) | Cu1 | O3 | C4 | C3 | -26.2(4) |
| N1 | C1 | C2 | O1 | 178.2(3) | Cu1 | O3 | C4 | Yb1[1] | 153.2(2) |
| N1 | C1 | C2 | O2 | -1.7(5) | N1 | C3 | C4 | O4 | 175.0(4) |
| C1 | N1 | C3 | C4 | -77.2(4) | N1 | C3 | C4 | O3 | -5.5(5) |
| Cu1 | N1 | C3 | C4 | 43.0(4) | | | | | |

[1]1-y,1-x,-1/2+z

**Table S7**. Unit-cell parameters refined by Le Bail fit for the powder X-ray diffraction patterns of CuLaIDA.

| $P\text{-}3c1$ | **Pristine crystals** | **After the first cycle** |
|---|---|---|
| $a$(Å) | 13.45202(5) | 13.423120(5) |
| $b$(Å) | 13.45202(5) | 13.423120(5) |
| $c$ Å) | 14.93527(7) | 14.953836(9) |
| $R_p$ | 11.6 | 9.98 |
| $R_{wp}$ | 14.8 | 13.1 |
| $\chi^2$ | 9.807 | 4.103 |

**Table S8**. Conversion and selectivity for the oxidation of cycloheptene and cyclooctene after 24h, using CuLaIDA as catalyst.

| Substrate | Conversion (%) | Selectivity (%) | | TOF |
|---|---|---|---|---|
| **Cycloheptene** | 53 | Cycloheptenone | 32 | 975 |
| | | Cycloheptenol | 18 | |
| | | Cycloheptene oxide | 43 | |
| | | Cycloheptanediol | 8 | |
| **Cyclooctene** | 45 | Cyclooctenone | - | 918 |
| | | Cyclooctenol | 10 | |
| | | Cycloctene oxide | 90 | |

***Reaction conditions: Temperature (75°C), Isobutyraldehyde (8 mmole), Catalyst (0.007 mmole), $Cu^{II}$ per mole of catalyst (0.13), Reaction time (24h), S/C ratio (5740/1 based on catalyst; 44000/1 based on $Cu^{II}$). [aldehyde]/[substrate] = 0.2***

**Table S9**. Conversion and selectivity for the oxidation of cyclohexene using different ratios of [aldehyde]/[cyclohexene].

| Ratio [RCHO]/[C6] | Conversion (%) | Selectivity (%) | |
|---|---|---|---|
| **0.2** | 73 | Cyclohexenone | 66 |
| | | Cyclohexenol | 30 |
| | | Cyclohexene oxide | 4 |
| **0.5** | 55 | Cyclohexenone | 37 |
| | | Cyclohexenol | 41 |
| | | Cyclohexene oxide | 22 |
| **1** | 34 | Cyclohexenone | 20 |
| | | Cyclohexenol | 29 |
| | | Cyclohexene oxide | 51 |
| **2** | 25 | Cyclohexenone | 22 |
| | | Cyclohexenol | 20 |
| | | Cyclohexene oxide | 58 |
| **3** | 13 | Cyclohexenone | 18 |
| | | Cyclohexenol | 22 |
| | | Cyclohexene oxide | 60 |

***Reaction conditions: Temperature (75°C), Isobutyraldehyde (variable), Catalyst (0.007 mmole), $Cu^{II}$ per mole of catalyst (0.13), Reaction time (24h), S/C ratio (5740/1 based on catalyst; 44000/1 based on $Cu^{II}$). [RCHO] = aldehyde; [C6] = cyclohexene.***

## References


1 C. S. Manna, S. Konar, E. Zangrando, J. Ribas and N. Ray, *Polyhedron*, 2007, **26**, 2507.

2 M. Xu, F. Liao, J. Li, H. Sun, Z. Li and S. Gao, *Inorg. Chem. Commun.*, 2003, **6**, 841.

3 R. Yan-ping, L. La-Sheng, M. Bing-Wei, Y. You-Zhu, H. Rong-bin and Z. Lan-Sun, *Angew. Chemie - Int. Ed.*, 2003, **42**, 1999.

4 J. Torres, P. Morales, S. Domínguez, J. González-Platas, R. Faccio, J. Castiglioni, A. W. Mombrú and C. Kremer, *J. Mol. Struct.*, 2011, **1004**, 215.

5 Y. Cai, G. Li, Q. Zhan, F. Sun, J. Zhang, S. Gao and A. Xu, *J. Solid State Chem.*, 2005, **178**, 3729.

6 J. Ma, X. Huang, X. Song, L. Zhou and W. Liu, *Inorganica Chim. Acta*, 2009, **362**, 3274.

7 L.-S. Long, Y. P. Ren, Y. Q. Jiang, L. F. Yang, R. B. Huang and L. S. Zheng, *CCDC 199860 Exp. Cryst. Struct. Determ.*

8 H. Cui, B. Zhou, L. Long, Y. Okano and H. Kobayashi, *Angew. Chemie - Int. Ed.*, 2008, **47**, 3376.

9 B. Zhou, A. Kobayashi, H. Cui, L. Long, H. Fujimori and H. Kobayashi, *J. Am. Chem. Soc.*, 2011, **133**, 5736.

10 R. D. Shannon, Acta Crystallogr., 1976, **A32,** 751.

11 P. Chotmongkolsap, T. Bunchuay, W. Klysubun and J. Tantirungrotechai, *Eur. J. Inorg. Chem.*, 2018, **2018**, 703.

12 Z. Li, S. Wu, H. Ding, D. Zheng, J. Hu, X. Wang, Q. Huo, J. Guan and Q. Kan, *new J. Chem.*, 2013, **5**, 1561.

13 Rodriguez-Carjaval, J., Roisnel, T., Mater. Sci. Forum, 2004, 443-444,123-126.

14 Roisnel, T., Rodriguez-Carvajal, J., Mater. Sci. Forum, 2001, 378-381, 118-123.