SUPPORTING INFORMATION

Exploring Host-Guest Interactions in the α-Zn₃(HCOO)₆ Metal-Organic Framework

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Table S1. Summary of crystallographic data for CO$_2$-loaded α-Zn$_3$(HCOO)$_6$.

| Description                        | Value                      |
|------------------------------------|----------------------------|
| Formula                            | C$_{6.25}$H$_6$O$_{12.50}$Zn$_3$ |
| Formula Weight [g/mol]             | 477.22                     |
| Crystal Color and Habit            | colourless prism           |
| Crystal System                     | monoclinic                 |
| Space Group                        | P 2$_1$/n                  |
| Temperature [K]                    | 120                        |
| $a$ [Å]                            | 11.3261(15)$^a$            |
| $b$ [Å]                            | 9.8210(14)$^a$             |
| $c$ [Å]                            | 14.4412(19)$^a$            |
| $\alpha$ [$^\circ$]                | 90                         |
| $\beta$ [$^\circ$]                 | 91.297(5)$^a$              |
| $\gamma$ [$^\circ$]                | 90                         |
| V [Å$^3$]                          | 1605.9(4)$^a$              |
| Z                                  | 4                          |
| F(000)                             | 934                        |
| $\rho$ [g/cm$^3$]                  | 1.974                      |
| $\lambda$(CuKα) [Å]               | 1.54178                    |
| $\mu$ [cm$^{-1}$]                  | 5.787                      |
| Max 2θ for data collection [$^\circ$] | 135.17                   |
| Measured fraction of data          | 0.973                      |
| Number of reflections measured     | 5024                       |
| Unique reflections measured        | 5024                       |
| $R_1$                              | 0.0303                     |
| $wR_2$                             | 0.0986                     |
| $R_1$ (all data)                   | 0.0306                     |
| $wR_2$ (all data)                  | 0.0992                     |
| GOF                                | 1.224                      |

$^a$Errors are given in parentheses

$$R_1 = \frac{\sum |F_o| - |F_c|}{\sum F_o}$$

$$wR_2 = \left[ \frac{\sum (w(F_o^2 - F_c^2)^2)}{\sum wF_o^4} \right]^{1/2}$$

$$GOF = \left[ \frac{\sum w(F_o^2 - F_c^2)^2}{(\text{No. of refin.} - \text{No. of params.})} \right]^{1/2}$$
Table S2. Atomic coordinates for CO₂-loaded α-Zn₃(HCOO)₆ obtained from X-ray diffraction. Errors are given in parentheses.

| Atom  | x         | y         | z         | U₁₁₁/equiv |
|-------|-----------|-----------|-----------|------------|
| Zn1   | 0.24331(4)| 0.07756(5)| 0.36832(3)| 0.00978(16)|
| Zn2   | 0.24050(4)| 0.39126(5)| 0.31300(3)| 0.01070(16)|
| Zn3   | 0.5000    | 0.0000    | 0.5000    | 0.01207(19)|
| Zn4   | 0.0000    | 0.0000    | 0.5000    | 0.01229(19)|
| O1    | 0.3157(2) | -0.0274(3)| 0.47692(18)| 0.0137(6) |
| C1    | 0.2572(4) | -0.1057(4)| 0.5306(3) | 0.0139(8) |
| O2    | 0.1496(2) | -0.1141(3)| 0.5339(2) | 0.0171(6) |
| O3    | 0.1025(2) | 0.1551(3) | 0.43955(18)| 0.0124(5) |
| C2    | 0.0706(4) | 0.2786(4) | 0.4488(3) | 0.0157(8) |
| O4    | 0.1118(2) | 0.3792(3) | 0.40880(19)| 0.0163(6) |
| O5    | 0.1919(2) | 0.1994(3) | 0.25419(18)| 0.0120(5) |
| C3    | 0.1699(3) | 0.1720(4) | 0.1697(3) | 0.0133(8) |
| O6    | 0.1833(2) | 0.0606(3) | 0.13111(19)| 0.0155(6) |
| O7    | 0.3472(2) | 0.2554(3) | 0.39048(19)| 0.0123(6) |
| C4    | 0.4222(4) | 0.2883(4) | 0.4533(3) | 0.0165(8) |
| O8    | 0.4814(2) | 0.2092(3) | 0.5024(2) | 0.0189(6) |
| O9    | 0.1494(2) | -0.0832(3)| 0.30488(18)| 0.0125(5) |
| C5    | 0.0458(4) | -0.1294(4)| 0.3133(3) | 0.0157(8) |
| O10   | -0.0234(2)| -0.1044(3)| 0.3761(2) | 0.0189(6) |
|     | a          | b          | c          | d          |
|-----|------------|------------|------------|------------|
| O11 | 0.3700(2)  | -0.0069(3) | 0.28039(18)| 0.0122(6)  |
| C6  | 0.4814(3)  | -0.0149(4) | 0.2878(3)  | 0.0136(8)  |
| O12 | 0.5411(2)  | 0.0035(3)  | 0.3596(2)  | 0.0192(6)  |
| C1x | -0.255(3)  | -0.251(5)  | 0.300(2)   | 0.137(18)  |
| O1x | -0.260(2)  | -0.298(4)  | 0.3736(19) | 0.124(12)  |
| O2x | -0.245(2)  | -0.173(3)  | 0.2402(17) | 0.109(10)  |
| H1  | 0.300(4)   | -0.158(4)  | 0.569(3)   | 0.004(9)   |
| H2  | 0.003(4)   | 0.292(5)   | 0.491(3)   | 0.006(10)  |
| H3  | 0.138(4)   | 0.249(4)   | 0.136(3)   | 0.008(11)  |
| H4  | 0.438(5)   | 0.392(7)   | 0.460(4)   | 0.045(17)  |
| H5  | 0.017(4)   | -0.189(5)  | 0.269(3)   | 0.008(10)  |
| H6  | 0.525(5)   | -0.040(6)  | 0.234(4)   | 0.031(14)  |

*Subscript X indicates CO₂ atoms*
Table S3. Anisotropic displacement parameters for CO$_2$-loaded $\alpha$-Zn$_3$(HCOO)$_6$. Errors are given in parentheses.

| Atom$^a$ | $u^{11}$     | $u^{22}$     | $u^{33}$     | $u^{12}$   | $u^{13}$   | $u^{23}$   |
|----------|--------------|--------------|--------------|------------|------------|------------|
| Zn1      | 0.0100(3)    | 0.0097(3)    | 0.0098(3)    | 0.00014(18)| 0.00347(19)| 0.00060(18)|
| Zn2      | 0.0115(3)    | 0.0101(3)    | 0.0106(3)    | -0.00007(18)| 0.00315(19)| 0.00103(18)|
| Zn3      | 0.0090(4)    | 0.0147(4)    | 0.0126(4)    | -0.0006(3) | 0.0019(3)  | 0.0013(3)  |
| Zn4      | 0.0104(4)    | 0.0134(4)    | 0.0133(4)    | -0.0014(3) | 0.0058(3)  | 0.0016(3)  |
| O1       | 0.0118(13)   | 0.0168(14)   | 0.0127(13)   | -0.0019(11)| 0.0038(10) | 0.0029(11) |
| C1       | 0.017(2)     | 0.013(2)     | 0.0118(19)   | -0.0002(15)| 0.0012(16) | 0.0031(15) |
| O2       | 0.0105(14)   | 0.0189(15)   | 0.0223(15)   | -0.0013(11)| 0.0064(11) | 0.0063(11) |
| O3       | 0.0128(12)   | 0.0091(14)   | 0.0158(13)   | 0.0012(11) | 0.0073(10) | 0.0015(11) |
| C2       | 0.0116(19)   | 0.023(2)     | 0.0124(19)   | 0.0003(16) | 0.0034(16) | 0.0006(17) |
| O4       | 0.0178(14)   | 0.0133(15)   | 0.0182(14)   | 0.0002(11) | 0.0076(11) | 0.0023(11) |
| O5       | 0.0151(13)   | 0.0092(14)   | 0.0119(13)   | -0.0010(11)| 0.0023(10) | -0.0003(10)|
| C3       | 0.0149(18)   | 0.014(2)     | 0.0105(18)   | 0.0024(15) | -0.0011(14)| 0.0013(15) |
| O6       | 0.0194(14)   | 0.0126(14)   | 0.0144(13)   | 0.0014(11) | -0.0010(11)| -0.0031(11)|
| O7       | 0.0104(14)   | 0.0155(15)   | 0.0112(14)   | 0.0007(9)  | 0.0003(11) | 0.0013(10) |
| C4       | 0.0155(19)   | 0.014(2)     | 0.020(2)     | -0.0030(16)| 0.0012(16) | -0.0013(17)|
| O8       | 0.0174(14)   | 0.0174(15)   | 0.0216(15)   | 0.0012(12) | -0.0034(12)| 0.0006(12) |
| O9       | 0.0116(13)   | 0.0124(14)   | 0.0137(13)   | -0.0017(10)| 0.0042(10) | -0.0014(10)|
| C5       | 0.016(2)     | 0.017(2)     | 0.015(2)     | -0.0056(16)| 0.0040(16) | -0.0033(16)|
| O10      | 0.0150(14)   | 0.0242(16)   | 0.0178(15)   | -0.0058(11)| 0.0081(12) | -0.0021(12)|
|          |     |     |     |     |     |     |
|----------|-----|-----|-----|-----|-----|-----|
| O11      | 0.0112(13) | 0.0114(14) | 0.0144(13) | 0.0002(10) | 0.0047(10) | -0.0025(10) |
| C6       | 0.0133(19) | 0.018(2)   | 0.0100(19) | -0.0007(15) | 0.0031(15) | 0.0005(15) |
| O12      | 0.0134(14) | 0.0303(18) | 0.0140(15) | 0.0002(11)  | 0.0016(11) | 0.0017(12) |
| C1_     | 0.036(18)  | 0.26(4)    | 0.12(2)    | 0.02(2)     | 0.020(17)  | 0.08(3)    |
| O1_     | 0.071(17)  | 0.20(3)    | 0.100(18)  | 0.01(2)     | 0.024(14)  | 0.05(2)    |
| O2_     | 0.056(13)  | 0.20(3)    | 0.074(14)  | -0.007(16)  | 0.000(11)  | 0.025(16)  |

*Subscript X indicates CO$_2$ atoms*
Table S4. Bond lengths (Å) for CO$_2$-loaded α-Zn$_3$(HCOO)$_6$. Errors are given in parentheses.

| Bond          | Length (Å) | Bond          | Length (Å) |
|---------------|------------|---------------|------------|
| Zn1-O1        | 2.034(3)   | O1-C1         | 1.286(5)   |
| Zn1-O3        | 2.063(3)   | C1-O2         | 1.224(5)   |
| Zn1-O9        | 2.102(3)   | C1-H1         | 0.89(5)    |
| Zn1-O11       | 2.108(3)   | O3-C2         | 1.273(5)   |
| Zn1-O5        | 2.108(3)   | C2-O4         | 1.241(5)   |
| Zn1-O7        | 2.126(3)   | C2-H2         | 1.00(5)    |
| Zn2-O6$^1$    | 2.033(3)   | O5-C3         | 1.269(5)   |
| Zn2-O4        | 2.036(3)   | C3-O6         | 1.238(5)   |
| Zn2-O11$^1$   | 2.076(3)   | C3-H3         | 0.97(5)    |
| Zn2-O7        | 2.105(3)   | O6-Zn$^2$     | 2.033(3)   |
| Zn2-O5        | 2.134(3)   | O7-C4         | 1.271(5)   |
| Zn2-O9$^1$    | 2.147(3)   | C4-O8         | 1.238(5)   |
| Zn3-O8        | 2.066(3)   | C4-H4         | 1.03(6)    |
| Zn3-O8$^2$    | 2.066(3)   | O9-C5         | 1.267(5)   |
| Zn3-O12$^2$   | 2.090(3)   | O9-Zn$^2$     | 2.147(3)   |
| Zn3-O12       | 2.090(3)   | C5-O10        | 1.236(5)   |
| Zn3-O1        | 2.124(3)   | C5-H5         | 0.92(5)    |
| Zn3-O1$^2$    | 2.124(3)   | O11-C6        | 1.266(5)   |
| Zn4-O10$^3$   | 2.074(3)   | O11-Zn$^2$    | 2.076(3)   |
| Zn4-O10       | 2.074(3)   | C6-O12        | 1.239(5)   |
| Zn4-O2$^3$    | 2.080(3)   | C6-H6         | 0.96(6)    |
|        |      |               |      |
|--------|------|---------------|------|
| Zn4-O2 | 2.080(3) | C1\textsubscript{1\textsuperscript{x}}-O1\textsubscript{1\textsuperscript{x}} | 1.161(7) |
| Zn4-O3 | 2.116(3) | C1\textsubscript{1\textsuperscript{x}}-O2\textsubscript{1\textsuperscript{x}} | 1.161(7) |
| Zn4-O3\textsuperscript{3} | 2.116(3) | | |

1. -x+1/2, y+1/2, -z+1/2
2. 1-x, -y,1+ -z
3.  -x, -y,1+ -z
4.  -x+1/2,-1+ y+1/2, -z+1/2

\textsuperscript{a}Subscript X indicates CO\textsubscript{2} atoms
Table S5. Bond angles (°) for CO$_2$-loaded $\alpha$-Zn$_3$(HCOO)$_6$. Errors are given in parentheses.

|bond| angle (°)          | probability | bond| angle (°)          | probability |
|-----|--------------------|-------------|-----|--------------------|-------------|
|O1-Zn1-O3| 96.05(10)       | O10-Zn4-O3| 93.48(10)       |
|O1-Zn1-O9| 98.42(11)       | O2$^3$-Zn4-O3| 88.08(10)       |
|O3-Zn1-O9| 96.05(10)       | O2-Zn4-O3| 91.92(10)       |
|O1-Zn1-O11| 89.84(11)      | O10$^3$-Zn4-O3$^3$| 93.48(10)       |
|O3-Zn1-O11| 172.00(11)      | O10-Zn4-O3$^3$| 86.52(10)       |
|O9-Zn1-O11| 77.68(10)       | O2$^3$-Zn4-O3$^3$| 91.92(10)       |
|O1-Zn1-O5| 171.92(10)      | O2-Zn4-O3$^3$| 88.08(10)       |
|O3-Zn1-O5| 88.68(10)       | O3-Zn4-O3$^3$| 180.0           |
|O9-Zn1-O5| 87.55(10)       | C1-O1-Zn1| 124.3(3)        |
|O11-Zn1-O5| 86.11(10)      | C1-O1-Zn3| 119.9(2)        |
|O1-Zn1-O7| 95.07(11)       | Zn1-O1-Zn3| 115.74(12)      |
|O3-Zn1-O7| 93.04(11)       | O2-C1-O1| 126.2(4)        |
|O9-Zn1-O7| 162.82(11)      | O2-C1-H1| 118(3)          |
|O11-Zn1-O7| 91.82(10)      | O1-C1-H1| 116(3)          |
|O5-Zn1-O7| 78.10(10)       | C1-O2-Zn4| 139.6(3)        |
|O6$^1$-Zn2-O4| 94.71(11)     | C2-O3-Zn1| 128.9(2)        |
|O6$^1$-Zn2-O11$^1$| 96.19(10)   | C2-O3-Zn4| 118.9(2)        |
|O4-Zn2-O11$^1$| 92.24(11)     | Zn1-O3-Zn4| 112.16(12)      |
|O6$^1$-Zn2-O7| 94.26(11)      | O4-C2-O3| 126.8(4)        |
|O4-Zn2-O7| 90.75(11)       | O4-C2-H2| 119(3)          |
|O11$^1$-Zn2-O7| 168.86(10)   | O3-C2-H2| 114(3)          |
|O6$^1$-Zn2-O5| 169.75(11)     | C2-O4-Zn2| 130.2(3)        |
|O4-Zn2-O5| 92.10(11)       | C3-O5-Zn1| 132.5(3)        |
|O11$^1$-Zn2-O5| 91.19(10)      | C3-O5-Zn2| 127.8(2)        |
|O7-Zn2-O5| 77.97(10)       | Zn1-O5-Zn2| 97.22(11)       |
|O6$^1$-Zn2-O9$^1$| 88.29(11)     | O6-C3-O5| 126.6(4)        |
|O4-Zn2-O9$^1$| 169.44(11)     | O6-C3-H3| 121(3)          |
|O11$^1$-Zn2-O9$^1$| 77.36(10)     | O5-C3-H3| 113(3)          |
|O7-Zn2-O9$^1$| 99.14(11)      | C3-O6-Zn2$^4$| 126.8(3)       |
|O5-Zn2-O9$^1$| 86.39(10)      | C4-O7-Zn2| 125.8(3)        |
| Bond                        | Angle (°) | Bond                        | Angle (°) |
|-----------------------------|-----------|-----------------------------|-----------|
| O8-Zn3-O8²                  | 180.0     | C4-O7-Zn1                   | 132.5(3)  |
| O8-Zn3-O12²                 | 88.59(11) | Zn2-O7-Zn1                  | 97.57(12) |
| O8²-Zn3-O12²                | 91.42(11) | O8-C4-O7                    | 126.4(4)  |
| O8-Zn3-O12                  | 91.41(11) | O8-C4-H4                    | 118(3)    |
| O8²-Zn3-O12                 | 88.58(11) | O7-C4-H4                    | 115(3)    |
| O12²-Zn3-O12                | 180.0     | C4-O8-Zn3                   | 132.0(3)  |
| O8-Zn3-O1                   | 91.62(11) | C5-O9-Zn1                   | 133.4(3)  |
| O8²-Zn3-O1                  | 88.38(11) | C5-O9-Zn2<sup>a</sup>       | 126.2(3)  |
| O12²-Zn3-O1                 | 84.87(10) | Zn1-O9-Zn2<sup>a</sup>     | 97.82(10) |
| O12-Zn3-O1                  | 95.13(10) | O10-C5-O9                   | 127.2(4)  |
| O8-Zn3-O1<sup>2</sup>       | 88.38(11) | O10-C5-H5                   | 114(3)    |
| O8²-Zn3-O1<sup>2</sup>      | 91.62(11) | O9-C5-H5                    | 119(3)    |
| O12²-Zn3-O1<sup>2</sup>     | 95.13(10) | C5-O10-Zn4                  | 131.3(3)  |
| O12-Zn3-O1<sup>2</sup>      | 84.87(10) | C6-O11-Zn2<sup>a</sup>     | 127.6(2)  |
| O1-Zn3-O1<sup>2</sup>       | 180.0     | C6-O11-Zn1                  | 131.6(3)  |
| O10³-Zn4-O10                | 180.0     | Zn2<sup>a</sup>-O11-Zn1    | 99.92(11) |
| O10³-Zn4-O2³                | 91.39(12) | O12-C6-O11                  | 125.9(4)  |
| O10-Zn4-O2³                 | 88.61(12) | O12-C6-H6                   | 116(3)    |
| O10³-Zn4-O2                 | 88.61(12) | O11-C6-H6                   | 118(3)    |
| O10-Zn4-O2                  | 91.39(12) | C6-O12-Zn3                  | 132.9(3)  |
| O2³-Zn4-O2                  | 180.0     | O1<sub>x</sub>C1<sub>x</sub>-O2<sub>x</sub> | 163(6) |
| O10³-Zn4-O3                 | 86.52(10) |                             |           |

1. -x+1/2, y+1/2, -z+1/2
2. 1-x, -y,1+ -z
3. -x, -y,1+ -z
4. -x+1/2,-1+ y+1/2, -z+1/2

<sup>a</sup>Subscript X indicates CO<sub>2</sub> atoms
Table S6. Torsion angles (°) for CO$_2$-loaded α-Zn$_3$(HCOO)$_6$. Errors are given in parentheses.

|       |       |       |       |
|-------|-------|-------|-------|
| Zn1-O1-C1-O2 | -11.3(6) | Zn2-O7-C4-O8 | 176.3(3) |
| Zn3-O1-C1-O2 | 168.1(3) | Zn1-O7-C4-O8 | 24.6(6)  |
| O1-C1-O2-Zn4 | -21.9(7) | O7-C4-O8-Zn3 | 6.4(7)   |
| Zn1-O3-C2-O4 | 7.7(6)  | Zn1-O9-C5-O10 | -14.2(7) |
| Zn4-O3-C2-O4 | -170.5(3) | Zn2$^1$-O9-C5-O10 | -171.9(3) |
| O3-C2-O4-Zn2 | 1.2(6)  | O9-C5-O10-Zn4 | -8.2(7)  |
| Zn1-O5-C3-O6 | -6.2(6) | Zn2$^1$-O11-C6-O12 | -151.9(3) |
| Zn2-O5-C3-O6 | 152.1(3) | Zn1-O11-C6-O12 | 15.1(6)  |
| O5-C3-O6-Zn2$^1$ | -6.5(6) | O11-C6-O12-Zn3 | 19.8(6)  |

1. -x+1/2,-y+1/2,-z+1/2
Table S7. Potential host-guest hydrogen bonds within CO$_2$-loaded α-Zn$_3$(HCOO)$_6$. Errors are given in parentheses.

| Hydrogen Bond  | D—H (Å) | H···A (Å) | D···A (Å) | D—H···A (°) |
|----------------|----------|-----------|-----------|-------------|
| C3-H3···O8$^1$ | 0.97(5)  | 2.62(5)   | 3.395(5)  | 137(3)      |
| C4-H4···O6$^2$ | 1.03(6)  | 2.51(6)   | 3.162(5)  | 121(4)      |
| C6-H6···O4$^3$ | 0.96(6)  | 2.67(5)   | 3.181(5)  | 114(4)      |

1. x-1/2,1+ -y-1/2, z-1/2
2. -x+1/2, y+1/2, -z+1/2
3. -x+1/2,-1+ y+1/2, -z+1/2
Table S8. The average O-Zn-O bond angles (°) and Zn-O distances (Å) in CO$_2$-loaded α-Zn$_3$(HCOO)$_6$ and activated Zn$_3$(HCOO)$_6$ for the four crystallographically inequivalent Zn. Errors are given in parentheses.

|        | CO$_2$-loaded α-Zn$_3$(HCOO)$_6$ | Activated Zn$_3$(HCOO)$_6^a$ |
|--------|---------------------------------|-----------------------------|
| Zn1-O  | 2.0905 (17)                     | 2.0901 (27)                 |
| Zn2-O  | 2.0892 (17)                     | 2.0885 (27)                 |
| Zn3-O  | 2.0953 (17)                     | 2.0934 (27)                 |
| Zn4-O  | 2.0901 (17)                     | 2.0898 (27)                 |
| O-Zn1-O| 89.88 (6)                       | 89.87 (10)                  |
| O-Zn2-O| 90.05 (6)                       | 90.05 (11)                  |
| O-Zn3-O| 90.00 (6)                       | 90.00 (11)                  |
| O-Zn4-O| 90.00 (6)                       | 90.00 (11)                  |

$^a$Data acquired from reference 1.
Figure S1. ORTEP drawing of the asymmetric unit of CO$_2$-loaded α-Zn$_3$(HCOO)$_6$ at 120 K. Ellipsoids are at the 50% probability level and hydrogens were drawn with arbitrary radii for clarity.
$^{67}\text{Zn} \text{ SSNMR Experimental Procedures}$

$^{67}\text{Zn} \text{ SSNMR experiments were performed at the National Ultrahigh-Field NMR Facility for Solids (www.nmr900.ca) using a Bruker Avance II NMR spectrometer ($B_0 = 21.1 \ T$, $\nu_0^{(67}\text{Zn}) = 56.29 \ MHz$). The static experiments were performed using a home-built 7 mm single-channel static probe. The magic-angle spinning (MAS) experiment was performed using a 4 mm Bruker H/X low gamma MAS probe. For all experiments, external chemical shift referencing and pulse calibration were performed using a 1.0 M aqueous $\text{Zn(NO}_3)_2$ solution ($\delta_{\text{iso}} = 0 \ ppm$). All spectra were recorded using a central-transition selective $\pi/2$ pulse width of 3 $\mu$s, which was determined by scaling the non-selective pulse length by $1/(l + 1/2)$ where $l = 5/2$ for $^{67}\text{Zn}$.

The static SSNMR spectra were acquired for the as-made, activate, $\text{CO}_2$-loaded and CO-loaded MOFs using a solid echo pulse sequence (i.e., $\pi/2 - \tau_1 - \pi/2 - \tau_2 - \text{acquire}$) with an inter-pulse delay ($\tau_1$) of 67 $\mu$s. For the as-made sample, the recycle delay was set to 0.25 s and 32 k scans were recorded. For the activated, $\text{CO}_2$-loaded and CO-loaded samples, a recycle delay of 1 s was used and 64 k scans were acquired. MAS experiment was also conducted on the as-made sample. A spinning speed of 15 kHz was employed, and the spectrum was obtained using a solid echo pulse sequence (i.e., $\pi/2 - \tau_1 - \pi/2 - \tau_2 - \text{acquire}$). An inter-pulse delay ($\tau_1$) of 63.6 $\mu$s was used. The recycle delay was set to 0.25 s, and 576 k scans were collected. Data were processed using TopSpin 2.1. The recorded FIDs were left-shifted to the echo maxima when needed.
Computational Details

$^{67}$Zn magnetic shielding and electric field gradient (EFG) tensors were calculated via the gauge-including projector-augmented wave (GIPAW) method using the NMR module of the CASTEP software package\textsuperscript{2-5} (version 4.4). The unit cell parameters and atomic coordinates were obtained from the crystal structure of $\alpha$-Zn$_3$(HCOO)$_6$:1/3HCO$_2$H.\textsuperscript{6} The solvent molecules were removed, and the resulting structure was geometry optimized by CASTEP. Two types of geometry optimization were performed: (a) the positions of all atoms are optimized and (b) the positions of the linker atoms are optimized and the positions of the metal centers were held fixed. For both geometry optimizations, the generalized gradient approximation functional of Perdew, Burke and Ernzerhof (GGA-PBE) was employed. “Ultrasoft” pseudopotentials, a plane-wave cutoff energy of 294 eV and a (1 x 1 x 1) $k$-point grind were used. The resulting optimized structures were used as inputs for the NMR calculations of the $^{67}$Zn magnetic shielding EFG tensors. A plane-wave cutoff energy of 294 eV, a (1 x 1 x 1) $k$-point grind, and “ultrasoft” pseudopotentials generated by the on-the-fly method were employed. The calculated isotropic magnetic shielding values ($\sigma_{\text{iso}}$) were converted into isotropic chemical shift ($\delta_{\text{iso}}$) values using the relation: $\delta_{\text{iso}}$ [ppm] = 1831.67 ppm - $\sigma_{\text{iso}}$ [ppm], where 1831.67 ppm is the absolute shielding for an infinitely dilute $^{67}$Zn$^{2+}$ ion in D$_2$O at 303 K.\textsuperscript{7-9} A nuclear quadrupole moment of 122 mb was used to generate the calculated quadrupolar coupling constants ($C_Q$).\textsuperscript{10, 11} The Euler angles between the magnetic shielding and EFG tensors were visualized using MagresView\textsuperscript{12} and the theoretical $^{67}$Zn SSNMR spectra were plotted using WSolids.\textsuperscript{13}
$^{67}$Zn SSNMR Results

To probe the local environment of the metal centers and the effect of adsorption of guest species on the Zn local structures, static $^{67}$Zn SSNMR experiments were performed for the as-made, activated, CO- and CO$_2$-loaded $\alpha$-Zn$_3$(HCOO)$_6$ (Figure S2). The spectra of the four samples look identical, suggesting that the presence of guest species inside the framework does not significantly alter the local Zn environments. This result is consistent with the crystallographic studies which show the Zn local geometry in as-made, the CO$_2$-loaded and activated frameworks are very similar. Furthermore, the crystal structures of the as-made, activated, and CO$_2$-loaded $\alpha$-Zn$_3$(HCOO)$_6$ indicate that there are four crystallographically inequivalent Zn sites in each phase with very similar local environments. This agrees with the observed $^{67}$Zn spectra, which contain multiple $^{67}$Zn signals severely overlapping with each other. No attempt was made to separate the individual resonances from different site via spectral simulation. For as-made $\alpha$-Zn$_3$(HCOO)$_6$, $^{67}$Zn MAS spectrum was also acquired. Only a relatively narrow signal was observed, confirming that the four Zn sites have very similar local structures.

To better understand the observed $^{67}$Zn spectra, $^{67}$Zn SSNMR parameters were calculated for the activated MOF by the DFT method. Two geometry optimized structures were used for calculation: (a) the positions of all atoms are optimized and (b) only the positions of the linker atoms are optimized and the positions of Zn atoms were held fixed. The calculated $^{67}$Zn NMR parameters are summarized in Table S9. For both structures, the absolute quadrupolar coupling constants ($|C_Q|$ s) for the four crystallographically inequivalent Zn were calculated to be within the range of ca. 4 to 8 MHz. The calculated asymmetry parameters ($\eta_Q$) were non-zero, consistent with the fact that none of the Zn lies on an $n$-fold rotation axis ($n \geq 3$). There are also small, but non-negligible chemical shift anisotropy (CSA) for each site. The calculations suggest that the observed static $^{67}$Zn spectra are mainly dominated by the second-order quadrupolar interaction with a minor contribution from the CSA.

The calculations based on the structure (a) indicate Zn1 and Zn2 have smaller $C_Q$ values, whereas the structure (b) predicts that Zn1 has the largest $C_Q$. Comparisons of the theoretical static and MAS spectra with the experimental ones suggest that the calculated $^{67}$Zn spectra based on structure (b) match the observed spectra slightly better. This implies that the geometrically optimized structure involving only the linker atoms more closely resembles the real structure. It appears that the broad “feet” in the static spectrum of the activated phase with a breath of ca. 50 kHz is due to Zn1.
Table S9. The calculated $^{67}$Zn EFG and chemical shift (CS) tensor parameters, and the Euler angles ($\alpha$, $\beta$, $\gamma$) describing the orientation of the CS and EFG principal axis systems for the four crystallographically inequivalent Zn atoms (Zn1, Zn2, Zn3 and Zn4) in the activated $\alpha$-Zn$_3$(HCOO)$_6$MOF.$^a$

|        | $\delta_{iso}$ (ppm) | $\Omega$ (ppm) | $\kappa$ | $|C_Q|^c$ (MHz) | $\eta_Q$ | $\alpha$ [$^\circ$] | $\beta$ [$^\circ$] | $\gamma$ [$^\circ$] |
|--------|----------------------|----------------|---------|----------------|----------|------------------|----------------|------------------|
| Zn1    | 297.1                | 46.2           | -0.30   | 5.1            | 0.96     | 33               | 70             | -1               |
| Zn2    | 321.1                | 101.1          | 0.22    | 4.3            | 0.11     | -61              | 59             | 41               |
| Zn3    | 288.4                | 69.1           | -0.03   | 8.2            | 0.39     | 94               | 154            | 4                |
| Zn4    | 293.5                | 94.1           | 0.50    | 6.9            | 0.95     | 69               | 153            | -82              |

Geometry Optimization Performed on Linker Atoms.$^b$

|        | $\delta_{iso}$ (ppm) | $\Omega$ (ppm) | $\kappa$ | $|C_Q|^c$ (MHz) | $\eta_Q$ | $\alpha$ [$^\circ$] | $\beta$ [$^\circ$] | $\gamma$ [$^\circ$] |
|--------|----------------------|----------------|---------|----------------|----------|------------------|----------------|------------------|
| Zn1    | 300.2                | 53.3           | -0.09   | 7.4            | 0.62     | 119              | 21             | -123             |
| Zn2    | 321.9                | 92.3           | 0.30    | 4.4            | 0.76     | 63               | 132            | -135             |
| Zn3    | 273.6                | 83.2           | 0.50    | 4.6            | 0.77     | 172              | 154            | 105              |
| Zn4    | 299.5                | 76.0           | 0.92    | 5.5            | 0.93     | 135              | 150            | -109             |

$^a$The input structure was obtained from the unit cell parameters and atomic coordinate of $\alpha$-Zn$_3$(HCOO)$_6$·1/3HCO$_2$H.$^6$ The solvent molecules were removed, and the positions of all atoms were geometry optimized.

$^b$The input structure was obtained from the unit cell parameters and atomic coordinate of $\alpha$-Zn$_3$(HCOO)$_6$·1/3HCO$_2$H.$^6$ The solvent molecules were removed, and the positions of the linker atoms were geometry optimized.
Figure S2. (a and b) The theoretical static $^{67}$Zn SSNMR spectra of activated $\alpha$-$\text{Zn}_3(\text{HCOO})_6$ shown as summations (black trace) of the Zn1 (red trace), Zn2 (gray trace), Zn3 (brown trace) and Zn4 (blue trace) resonances. (a) was acquired after geometry optimizing the positions of all atoms, while (b) was acquired after geometry optimizing the positions of the linker atoms. The calculated EFG and CS tensor parameters are also provided in Table S9. The experimental static $^{67}$Zn SSNMR spectra of (c) activated, (d) CO$_2$-loaded, (e) CO-loaded and (f) as-made $\alpha$-$\text{Zn}_3(\text{HCOO})_6$ acquired at 21.1 T.
Figure S3. Theoretical (a and b) and experimental (c) $^{67}$Zn SSNMR spectra of as-made α-Zn$_3$(HCOO)$_6$. (a) was acquired after geometry optimizing the positions of all atoms, while (b) was acquired after geometry optimizing the positions of the linker atoms. The experimental spectrum was acquired at 15 kHz and 21.1 T.
Figure S4. The local pore structure of CO$_2$-loaded α-Zn$_3$(HCOO)$_6$, as viewed from different perspectives. 
(a) Shows the distances between the carbon of the CO$_2$ and the closest framework oxygens, while (b) shows the distance between one of the oxygens (O1) of CO$_2$ and two closest framework hydrogens (H2 and H4). Carbons are grey, oxygens are red, hydrogens are white and [ZnO$_6$] units are depicted as purple octahedra. Errors associated with the distances are provided in parentheses.
Table S10. The apparent $^{13}$C CS tensor parameters ($\delta_{\text{iso}}$, $\Omega$ and $\kappa$) and motional angles ($\alpha$ and $\beta$) of CO$_2$ adsorbed in $\alpha$-Zn$_3$(HCOO)$_6$ at temperatures ranging from 123 to 433 K. The CS tensor parameters were obtained from analytical simulations, and the angles were acquired from motional simulations. All motions occur at rates on the order of magnitude of ca. $\geq 10^7$ Hz in the considered temperature range.

| Temperature [K] | $\delta_{\text{iso}}$ [ppm] | $\Omega$ [ppm] | $\kappa$ | $\alpha$ [$^\circ$] | $\beta$ [$^\circ$] |
|-----------------|------------------|---------------|--------|-----------------|-----------------|
| 433             | 126.0 ± 1.0      | 36.3 ± 2.0    | -0.42 ± 0.02 | 47.5 ± 0.5 | 40.0 ± 0.5 |
| 413             | 126.5 ± 0.5      | 35.5 ± 1.0    | -0.38 ± 0.05 | 47.5 ± 0.5 | 39.0 ± 0.5 |
| 393             | 126.3 ± 0.5      | 34.0 ± 0.5    | -0.38 ± 0.05 | 47.5 ± 0.5 | 39.0 ± 0.5 |
| 373             | 126.1 ± 0.5      | 32.0 ± 0.5    | -0.46 ± 0.02 | 48.0 ± 0.5 | 40.0 ± 0.5 |
| 353             | 126.2 ± 0.5      | 29.5 ± 0.5    | -0.51 ± 0.02 | 48.0 ± 0.5 | 40.0 ± 0.5 |
| 333             | 126.3 ± 0.5      | 27.7 ± 0.5    | -0.61 ± 0.03 | 49.0 ± 0.5 | 41.5 ± 0.5 |
| 313             | 126.2 ± 0.5      | 24.5 ± 0.5    | -0.76 ± 0.02 | 49.5 ± 0.5 | 43.5 ± 0.5 |
| 293             | 126.2 ± 0.5      | 22.5 ± 0.5    | -0.96 ± 0.02 | 49.5 ± 0.5 | 47.0 ± 0.5 |
| 273             | 126.2 ± 0.5      | 23.0 ± 1.0    | -0.74 ± 0.02 | 49.5 ± 0.5 | 42.5 ± 0.5 |
| 253             | 126.0 ± 0.5      | 26.5 ± 1.0    | -0.40 ± 0.02 | 49.0 ± 0.5 | 39.5 ± 0.5 |
| 233             | 125.9 ± 0.5      | 32.0 ± 1.0    | -0.02 ± 0.02 | 49.0 ± 0.5 | 36.0 ± 0.5 |
| 213             | 125.7 ± 0.5      | 40.5 ± 1.0    | 0.21 ± 0.02  | 48.0 ± 0.5 | 32.0 ± 0.5 |
| 193             | 125.5 ± 0.5      | 53.0 ± 1.0    | 0.37 ± 0.02  | 47.0 ± 0.5 | 30.5 ± 0.5 |
| 173             | 126.3 ± 0.5      | 70.0 ± 1.0    | 0.46 ± 0.02  | 44.0 ± 0.5 | 28.6 ± 0.5 |
| 153             | 125.5 ± 0.5      | 89.8 ± 1.0    | 0.53 ± 0.02  | 42.0 ± 0.5 | 26.0 ± 0.5 |
| 133             | 125.5 ± 0.5      | 112.0 ± 1.0   | 0.56 ± 0.02  | 40.0 ± 0.5 | 24.5 ± 0.5 |
| 123             | 125.5 ± 0.5      | 128.0 ± 1.0   | 0.55 ± 0.02  | 37.0 ± 0.5 | 25.0 ± 0.5 |
Table S11. The observed $^{13}$C CS tensor parameters ($\delta_{\text{iso}}$, $\Omega$ and $\kappa$) and motional angles ($\alpha$ and $\theta$) of CO adsorbed in $\alpha$-Zn$_3$(HCOO)$_6$ at various temperatures ($T = 173$ to 433 K). The $^{13}$C CS tensor parameters and the motional angles were obtained from analytical and motional simulations, respectively. All motions occur at rates on the order of magnitude of ca. $\geq 10^7$ Hz in the experimental temperature range.

| Temperature [K] | $\delta_{\text{iso}}$ [ppm] | $\Omega$ [ppm] | $\kappa$ | $\alpha$ [$^\circ$] | $\theta$ [$^\circ$] |
|-----------------|-----------------|-----------------|----------|----------------|----------------|
| 433             | 184.0 ± 0.5     | 41.0 ± 2.0      | -0.40 ± 0.05 | 47.5 ± 0.5    | 39.5 ± 0.5    |
| 413             | 183.3 ± 0.5     | 43.0 ± 2.0      | -0.30 ± 0.05 | 47.0 ± 0.5    | 38.5 ± 0.5    |
| 393             | 184.0 ± 0.5     | 46.0 ± 2.0      | -0.25 ± 0.05 | 47.0 ± 0.5    | 37.5 ± 0.5    |
| 373             | 184.0 ± 0.5     | 46.0 ± 2.0      | -0.15 ± 0.05 | 46.5 ± 0.5    | 37.0 ± 0.5    |
| 353             | 183.3 ± 0.5     | 48.0 ± 1.0      | -0.05 ± 0.05 | 46.5 ± 0.5    | 35.5 ± 0.5    |
| 333             | 183.0 ± 0.5     | 49.8 ± 1.0      | -0.02 ± 0.05 | 46.5 ± 0.5    | 35.5 ± 0.5    |
| 313             | 183.0 ± 0.5     | 50.5 ± 1.0      | 0.05 ± 0.02 | 46.5 ± 0.5    | 35.0 ± 0.5    |
| 293             | 184.0 ± 0.5     | 56.0 ± 1.0      | 0.32 ± 0.02 | 46.0 ± 0.5    | 29.5 ± 0.5    |
| 273             | 184.0 ± 0.5     | 58.5 ± 1.0      | 0.44 ± 0.02 | 46.0 ± 0.5    | 28.0 ± 0.5    |
| 233             | 183.6 ± 0.5     | 65.0 ± 1.0      | 0.66 ± 0.02 | 46.0 ± 0.5    | 23.0 ± 0.5    |
| 213             | 184.0 ± 0.5     | 65.0 ± 1.0      | 1 - 0.02   | 46.0 ± 0.5    | 20.0 ± 0.5    |
| 193             | 184.0 ± 0.5     | 70.0 ± 1.0      | 1 - 0.02   | 45.5 ± 0.5    | 20.0 ± 0.5    |
| 173             | 183.0 ± 0.5     | 77.0 ± 1.0      | 1 - 0.02   | 45.0 ± 0.5    | 20.0 ± 0.5    |
Figure S5. Charts illustrating changes in the (a and b) apparent $^{13}$C CS tensor parameters ($\Omega$ and $\kappa$) and (c and d) motional angles ($\alpha$ and $\beta$) of CO$_2$ adsorbed in $\alpha$-Zn$_3$(HCOO)$_6$ as a function of temperature. The values are also tabulated in Table S10.
Figure S6. Illustration of the (left) wobbling and (right) hopping motions exhibited by CO in α-Zn₃(HCOO)₆. α and β describe the wobbling and hopping angles, respectively. Carbons are dark grey, oxygens are red, hydrogens are white and [ZnO₆] units are purple octahedra. The [ZnO₆] units that connect the top and the bottom of the channels were omitted for clarity. The red and grey dashed lines represent C-O bonds between the carbons and the omitted [ZnO₆] units. All framework carbons and hydrogens are also omitted for clarity except for H1, H5 and H6 and the corresponding carbons.
Figure S7. A comparison between the motional angles ($\alpha$ and $\beta$) of CO$_2$ (open red circles) and CO (solid black squares) in $\alpha$-Zn$_3$(HCOO)$_6$ at various temperatures. The temperature where the $\alpha$ and $\beta$ trends begin to reverse for CO$_2$ (ca. 293 K) is marked with a solid dashed line. $\alpha$ and $\beta$ were acquired via motional simulations as shown in Figures 4 and 9. The values are also given in Tables S10 and S11.
Figure S8. Experimental PXRD patterns of as-made (red trace) and activated (blue trace) \(\alpha\)-Zn\(_3\)(HCOO)\(_6\) and the corresponding theoretical PXRD patterns (black trace for activated, green trace for as-made) constructed using previously reported crystal structures.\(^1\)
The Influence of Temperature on the Motional Rates of CO$_2$ in α-Zn$_3$(HCOO)$_6$

Figure S9 shows the spectra simulated for CO$_2$ in α-Zn$_3$(HCOO)$_6$ using a wobbling angle of 47.5° and a hopping angle of 40.0°. The simulated spectrum using rates of ca. $\geq 10^7$ Hz for both motions is in excellent agreement with the experimental spectrum acquired at 433 K (see Figure 4). Thus, CO$_2$ undergoes a 47.5° wobbling and a 40.0° hopping at rates of ca. $\geq 10^7$ Hz at 433 K. A decrease in temperature can result in a decrease in motional rates; however, we were unable to reproduce the experimental spectra acquired at $T < 433$ K using the same motional angles at slower motional rates. The experimental spectra were only successfully reproduced when the motional angles were varied with the motions occurring at ca. $\geq 10^7$ Hz. Thus, a decrease in temperature results in a change in the motional angles instead of motional rates.

Figure S9. Static $^{13}$CO$_2$ SSNMR spectra modelled using different motional rates. (a) The wobbling and hopping rates were varied from 0 to $10^8$ Hz. (b) The hopping rate was fixed at $10^7$Hz while the wobbling rate was varied from 0 to $10^8$ Hz. (c) The wobbling rate was fixed at $10^7$ Hz while the hopping rate was varied from 0 to $10^8$ Hz. Note in (a), (b), and (c), no change in lineshape was observed at rates $\geq 10^7$ Hz. All spectra were simulated using a wobbling angle of 47.5° and a hopping angle of 40.0°.
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