Supporting Information for

Lattice-Imposed Geometry in Metal-Organic Frameworks:

Lacunary Zn₄O Clusters in MOF-5 Serve as Tripodal Chelating Ligands for Ni²⁺

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Experimental details

Materials. Dichloromethane (HPLC grade, Honeywell), *N*,*N*-dimethylformamide (99.8%, VWR), Ni(NO₃)₂·6H₂O (99.9%, Strem), and Zn(NO₃)₂·6H₂O (99%, Alfa Aesar) were used as received. Mesityl-nitrile-*N*-oxide (MesCNO) was prepared according to published procedures.¹

X-ray crystal structure determination. A diffraction-quality single crystal of $Ni_{0.36}Zn_{3.64}O(BDC)_3$ was mounted on Kapton loops using paratone-N oil. Low temperature (100 K) diffraction data (φ - and ω -scans) were collected on a Bruker-AXS X8 Kappa Duo diffractometer coupled to a Smart APEX II CCD detector with Mo-K_{α} radiation ($\lambda = 0.71073$ Å) from a *IµS*-micro source. Absorption and other corrections were applied using SADABS.² The structures were solved by direct methods using SHELXS³ and refined against *F*² on all data by full-matrix least squares as implemented in SHELXL-97.² All non-hydrogen atoms were included at geometrically calculated positions using a riding model. The crystallographic data for Ni_{0.36}Zn_{3.64}O₁₃C₂₄H₁₂ is shown in Table S1.

Other physical measurements. Thermogravimetric analysis (TGA) was performed on a TA Instruments Q500 Thermogravimetric Analyzer at a heating rate of 0.5 °C/min under a nitrogen gas flow of 9 mL/min. Infrared spectra were obtained on a PerkinElmer Spectrum 400 FT-IR/FT-FIR Spectrometer equipped with a Pike Technologies GladiATR accessory with a diamond single-bounce crystal. Powder X-ray diffraction (PXRD) patterns were recorded on PANalytical X'Pert Pro and Bruker Advance II diffractometers equipped with $\theta/2\theta$ Bragg-Brentano geometry and Ni-filtered Cu-K_a radiation (K α_1 = 1.5406 Å). The tube voltage and current were 45 kV and 40 mA, respectively. Samples for PXRD were prepared by placing a thin layer of samples on a zero-background silicon crystal plate. Solution UV-Vis spectra were obtained at room temperature on an Agilent 8453 spectrophotometer. Diffuse reflectance UV-Vis spectra were collected on a Varian Cary 5000 UV-Vis-NIR spectrometer equipped with a Praying Mantis diffuse reflectance accessory and an environmental chamber (Harrick Scientific Products) and referenced to Spectralon® or BaSO₄.

A Micromeritics ASAP 2020 Surface Area and Porosity Analyzer was used to measure nitrogen adsorption isotherms. Oven-dried sample tubes equipped with TranSealsTM (Micrometrics) were evacuated and tared. Samples were transferred to the sample tubes, heated to the appropriate temperatures (as determined by TGA analysis), and held at those temperatures until the outgas rate was less than 2 mtorr/minute. The evacuated sample tubes were weighed again and the sample mass was determined by subtracting the mass of the previously tared tube. N₂ isotherms were measured using liquid nitrogen baths (77 K). UHP grade (99.999% purity) N₂ and He, oil-free valves and gas regulators were used for all free space corrections and measurements.

Magnetic data were collected using a Quantum Design MPMS-XL SQUID magnetometer. A gelatin capsule was filled with evacuated crystals of $Ni_{0.36}Zn_{3.64}O(BDC)_3$ to obtain susceptibility data. DC susceptibility measurements were obtained under a DC field of 100 Oe between 5 K – 300 K. All data was corrected for diamagnetic contributions from the capsule and the sample using Pascal's constants.⁴

Nickel and zinc analyses were conducted at the MIT Center for Materials Science and Engineering Shared Experimental Facility (CMSE-SEF) using a HORIBA Jobin ACTIVA inductively coupled plasma atomic emission spectrometer (ICP-AES). Standards were prepared from solutions purchased from ULTRA Scientific©, designated suitable for ICP analysis. The samples consisted of 5% HNO₃ solutions containing Ni-MOF-5 at concentrations in the range of 5 mg (metal) / L. To prepare these solutions, Ni-MOF-5 samples were added to the appropriate volume (~ 500 μ L) of 70% HNO₃, heated at 100 °C until complete dissolution, and diluted with deionized water to obtain a 5% HNO₃ solution.

Calculations. All time-dependent density functional theory (TD-DFT) calculations and geometry optimizations were performed at the spin-unrestricted level using the Becke-Perdew (BP) functional^{5,6} with the ORCA 2.8.0 software package.⁷ For each TD-DFT calculation, 10 excited states were included using one electron transitions. All geometry optimizations began from crystallographically-determined structures, where all atomic positions were optimized.

The all-electron Gaussian basis sets developed by the Ahlrichs group were employed in all calculations.^{8,9} The standard basis sets TZV(p) (for H), TZV(2d) (for C, N, and O), and TZV(2pf) (for Zn and Ni) were employed. The resolution of the identity (RI) approach was taken

for geometry optimizations, though not for TD-DFT calculations. The zeroth-order regular approximation (ZORA)^{10,11,12, 13} method was implemented for all calculations involving Ni.

Preparation of Ni-MOF-5. *Method A.* $Zn(NO_3)_2$ ·6H₂O (446 mg, 1.50 mmol), Ni(NO_3)_2·6H_2O (327 mg, 1.13 mmol), and terephthalic acid (H₂BDC, 83 mg, 0.50 mmol) were combined in a 100 mL jar with a Teflon-lined lid. The contents were dissolved in 49 mL of anhydrous DMF and 1 mL of deionized H₂O. The solution was heated for 7 h at 100 °C to afford yellow cubic crystals. The reaction container was allowed to cool to room temperature, then transferred to a nitrogen-filled glove bag, with oven-dried glassware and dry solvents. The crystals were collected by gravity filtration and washed with anhydrous DMF (6 × 20 mL), soaking for 8 h each time. The DMF was decanted and the resulting solid was washed with CH₂Cl₂ (6 × 20 mL), again soaking for 8 h after each wash. A UV-Vis spectrum was taken of the final DMF wash to verify the removal of free metal ions. After the final CH₂Cl₂ wash, the solvent was decanted and the crystals were heated under vacuum for 12 h (4 mtorr, 200 °C) to yield blue-purple crystals. ICP-AES and elemental microanalysis for C₂₄H₁₂O₁₃Ni_{0.36}Zn_{3.64}: Calculated: C% 37.60, H% 1.60, N% 0.00; Ni/Zn, 0.10 Found: C% 37.40, H% 1.80, N% 0.00; Ni/Zn, 0.10.

Method B. A sample of $Ni_xZn_{4-x}O(BDC)_3$ (x = 1) was obtained by soaking colorless MOF-5 crystals prepared in a manner described by Kaye et al.¹⁴ in a 20 mL solution of anhydrous DMF and 5.00 g Ni(NO₃)₂·6H₂O for ~ 1 year. Yellow cubic crystals were collected by decanting the solution. These were washed with DMF and CH₂Cl₂ in a manner identical to Method A. Ni-MOF-5 was obtained alternatively by soaking MOF-5 crystals for 2 weeks, but the Ni:Zn content never reached 1:3.

Preparation of (MesCNO)_{0.23}**Ni**_{0.23}**Zn**_{3.77}**O(BDC)**₃ and other Ni-MOF-5 adducts. A 15 mL toluene solution of MesCNO (11.4 mg, 70.5 μ mol) was added dropwise to a suspension of activated single crystals of Ni-MOF-5 (Ni_{0.23}Zn_{3.77}O₁₃C₂₄H₁₂) (150 mg, 0.196 mmol) in 5 mL of toluene under stirring at 35 °C. After combining, the mixture was allowed to warm to room temperature, whereupon the blue-purple crystals turned orange. Toluene was removed under

reduced pressure. Elemental microanalysis for $(C_{10}H_{11}NO)_{0.23}Ni_{0.23}Zn_{3.77}O_{13}C_{24}H_{12}(C_7H_8)_{3.5}$: Calculated: C% 54.10 H% 3.81 N% 0.29 Found: C% 54.72 H% 4.32 N% 0.10.

	$Ni_{0.36}Zn_{3.64}O_{13}C_{24}H_{12}$
Formula	C ₆ H ₃ N ₄ Ni _{0.09} O _{3.25} Zn _{0.91}
FW	247.91
Т, К	100(2)
group	Fm3m
Z	32
<i>a</i> , Å	25.8380(2)
$V, Å^3$	17249.5
d_{calc} , g/cm ³	0.784
μ, mm^{-1}	1.220
<i>F</i> (000)	3930
crystal size, mm	0.2x0.2x0.2
theta range	1.37 to 26.82
index ranges	$-32 \le h \le 32$
	$-32 \le k \le 32$
	$-32 \le l \le 32$
refl. collected	80165
data/restr./param.	991/0/34
GOF on F^2	1.571
largest peak/hole, e/Å ³	2.05/-0.45
<u>$R_1(wR_2), \% [I > 2 sigma(I)]^b$</u>	9.05 (34.24)

Table S1. Crystallographic data^{*a*} for evacuated crystals of Ni_{0.36}Zn_{3.64}O₁₃C₂₄H₁₂.

^a Mo-K α ($\lambda = 0.71073$ Å) radiation ^b R₁ = $\Sigma ||F_o| - |F_c|| / \Sigma |F_o|$, $wR_2 = \{ \Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2] \}^{1/2}$

Equation 1. The theoretical dependence of transitions ${}^{3}T_{1}(F) - {}^{3}A_{2}(\upsilon_{2})$ and ${}^{3}T_{1}(F) - {}^{3}T_{1}(P)(\upsilon_{3})$ on parameters B and Dq.

$$v_{2} = 15Dq - 7.5B + \frac{1}{2}(225B^{2} + 100Dq^{2} + 180DqB)^{\frac{1}{2}}$$
$$v_{3} = (225B^{2} + 100Dq^{2} + 180DqB)^{\frac{1}{2}}$$

Equation 2. The secular determinant for the mixing of the two ${}^{3}T_{1}$ terms by the tetrahedral ligand field. *Dq* and *B* are the ligand field and Racah parameters. Solving for E yields the relative energies of the ${}^{3}F$ and ${}^{3}P$ terms, E₁ and E₂.

$\Psi^0[{}^3T_1(F)]$	$\Psi^{0}[{}^{3}T_{1}(P)]$
-6 <i>Dq</i> - E	4Dq
4Dq	15 <i>B</i> – E

Equation 3. The wavefunction of the lowest ${}^{3}T_{1}$ term. $\Psi^{0}[{}^{3}T_{1}(F)] = (1 + c^{2})^{-1/2}(\Psi^{0}[{}^{3}T_{1}(F)] + c \Psi^{0}[{}^{3}T_{1}(P)])$

Equation 4. The definition of the mixing coefficient c. $c = 1.5 + E_1/4Dq$

Equation 5. The spin-only Hamiltonian used to fit the molar magnetic susceptibility data. $H = H_{ZFS} + H_{Zee} \quad \text{where}$ $H_{ZFS} = \sum_{i=1}^{ns} D_i [S_{z,i}^2 - \frac{1}{3}Si(Si + 1) + \frac{E_i}{D_i}(S_{x,i}^2 - S_{y,i}^2)]$ $H_{Zee} = \sum_{i=1}^{ns} g\beta S_i \cdot \beta$



Figure S1. Powder X-ray diffraction patterns of **Ni-MOF-5**. Differences in intensity between the as-synthesized and evacuated **Ni-MOF-5** are due to orientation effects. These occurred because the samples were prepared without grinding to avoid decomposition in the presence of moisture.



Figure S2. Formula of Ni-MOF-5 as a function of the initial molar ratio of Ni:Zn used in the preparation. Higher initial ratios of Ni:Zn leads to phase segregation and isolation of a yet unidentified green crystalline powder that does not match that of MOF-5 or any known Ni-BDC or Zn-BDC phases.



Figure S3. TGA plot of (DMF)_{0.72}Ni_{0.36}Zn_{3.64}O(BDC)₃.



Figure S4. FT-IR spectrum of as-synthesized **Ni-MOF-5** after washing with DMF and CH_2Cl_2 (A) and after evacuation (B), confirming the disappearance of the DMF carbonyl stretch.



Figure S5. Diffuse-reflectance UV-Vis-NIR spectra of (DMF)Ni-MOF-5 and of (MesCNO)Ni-MOF-5.



Figure S6. FT-IR spectrum of fully activated **Ni-MOF-5** (A) and (**MesCNO**)**Ni-MOF-5** (B). The CN stretch of the adduct is highlighted at 2293 cm⁻¹. Inset: Magnification of the region between 1500 cm⁻¹ and 1300 cm⁻¹ to emphasize the peaks at 1380 cm⁻¹ and at 1376 cm⁻¹. These appear as shoulders on the asymmetric carboxylate stretch and correspond to the C-H bend of the mesityl methyl groups and the N-O stretch of MesCNO.



Figure S7. Experimental diffuse-reflectance traces of the six-(yellow), five-(red), and four-(blue)-coordinate nickel(II) species are compared to the calculated transitions of their corresponding model compounds.



Figure S8. The experimental red trace of the purported $(DMF)_x Ni_x Zn_{4-x} O(BDC)_3$ is compared to two model compounds, where the nickel center is five-coordinate with a DMF bound axially or equatorially with respect to the carboxylate oxygens around nickel. See figure S11 for depictions of the model structures.

Relative Pressure (P/P ₀) at 77 K	Quantity Adsorbed (cm ³ /g)
0.0000214	19.98243
0.0000505	39.73469
0.0000966	59.11122
0.00018	77.75762
0.000344	94.90068
0.000628	109.385
0.001196	128.2154
0.001776	146.9999
0.002268	166.0054
0.002669	185.2003
0.002992	204.5732
0.003257	224.0812
0.003477	243.6969
0.003663	263.3969
0.003823	283.1579
0.003965	302.9673
0.004094	322.8039
0.004214	342.6673
0.004329	362.5358
0.004439	382.4163
0.004559	402.2755
0.004677	422.1226
0.004804	441.9529
0.004943	461.6088
0.005098	481.4293
0.005283	501.1614
0.005503	520.894
0.005771	540.3873
0.006099	559.6978
0.006526	578.8513
0.007059	597.5016
0.007779	616.0205
0.008718	633.82
0.009941	650.5231
0.011528	665.7543
0.013484	679.4467
0.016179	692.9824
0.019495	704.7982
0.023429	714.954
0.027919	723.6263

Table S1. N_2 adsorption data for $\ensuremath{\text{Ni-MOF-5}}$.

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0.03298	731.1561
0.038502	737.5712
0.044254	743.0649
0.050168	747.7704
0.096425	769.6294
0.202527	794.0204
0.305664	810.9348
0.400248	819.1817
0.499422	822.9535
0.618649	824.7154
0.718829	825.1492
0.818852	825.144
0.918734	825.043



Figure S9. N_2 adsorption isotherm for blue **Ni-MOF-5** at 77 K. The BET apparent surface area is 3300(100) m²/g. Eleven relative pressure points between 0.01 and 0.05 were chosen for the fit, giving a C value of 869.



Figure S10. Two views of the geometry-optimized cluster $NiZn_3O(O_2C-C_6H_5)_6$. Orange, green, red, grey, and white atoms represent Ni, Zn, O, C, H respectively.



Figure S11. Two stereoisomers of $(DMF)NiZn_3O(O_2C-C_6H_5)_6$ after geometry optimization. Orange, green, red, blue, grey, and white atoms represent Ni, Zn, O, N, C, and H respectively. The axial (left) and equatorial (right) geometries were juxtaposed the red experimental trace in figure S8. Scheme 1 and figure S7 employ the equatorial isomer as the better suited model for (DMF)Ni-MOF-5.



Figure S12. The geometry-optimized cluster $(DMF)_2NiZn_3O(O_2C-C_6H_5)_6$ that was used as a model for $(DMF)_2Ni-MOF-5$. Orange, green, red, blue, grey, and white atoms represent Ni, Zn, O, N, C, and H respectively.

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