

Supplementary Material

Compressing the Channels in the Crystal Structure of Copper Squarate Metal-Organic Framework

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Table S1. Interatomic distances in copper squarate (in Å). The atom numbering convention used for the oxygen atoms in the coordination environment of copper atom is shown in Figure S1.

| Distance | Exp. [1] | Calc. (PBEsol) |
|--------------|----------|----------------|
| Cu-O | | |
| Cu-O1 × 2 | 1.893(3) | 2.022 |
| Cu-O2 × 2 | 1.945(3) | 2.043 |
| Cu-O2* × 2 | 2.412(2) | 2.329 |
| Cu-Cu | | |
| Cu-Cu(min) | 3.289(1) | 3.216 |
| C-C | | |
| C1-C2 | - | 1.483 |
| C1-C2' | - | 1.493 |
| <C-C> | 1.447(2) | 1.488 |
| C-O | | |
| C1-O1 | - | 1.242 |
| C2-O2 | - | 1.254 |
| <C-O> | 1.234(3) | 1.248 |

Table S2. Interatomic angles in copper squarate (in degrees). The atom numbering convention used for the oxygen atoms in the coordination environment of copper atom is shown in Figure S1.

| Angle | Exp. [1] | Calc. |
|---------------------|-------------|--------|
| O-Cu-O | | |
| O1-Cu-O1' (cis) | 91.90(9) | 88.55 |
| O1-Cu-O2' (trans) | 177.10(11) | 176.31 |
| O2-Cu-O2* (cis) | 82.56.10(9) | 85.50 |
| O2*-Cu-O2*' (trans) | 167.83(8) | 171.25 |
| C-C-C | | |
| C1-C2-C1 | - | 90.51 |
| C2-C1-C2 | - | 89.49 |
| C-C-O | | |
| O1-C1-C2 | - | 132.12 |
| C1-C2-O2 | - | 131.90 |

Figure S1. The coordination environment of copper atom in copper squarate.

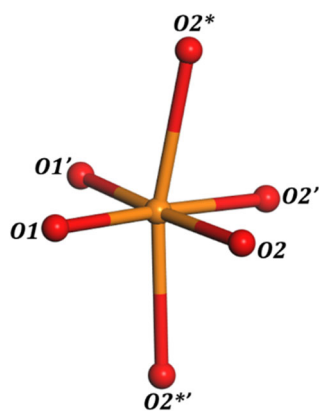


Figure S2. X-ray powder diffraction patterns of copper squarate generated from the computed and experimental [1] crystal structures.

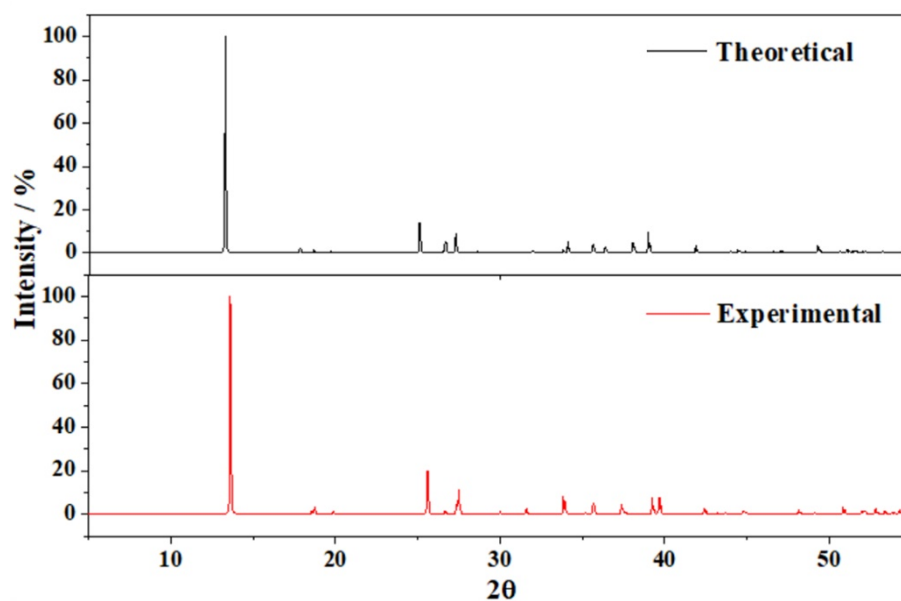


Table S3. Comparison of the positions and intensities of the most intense reflections in the calculated and experimental [1] X-ray powder diffraction patterns of copper squarate.

| $[h\ k\ l]$ | Exp. [1] | | | Calc. | | | |
|-------------|-----------------|---------|--------|-----------------|---------|--------|------------------------|
| | 2θ (deg) | d (Å) | I (%) | 2θ (deg) | d (Å) | I (%) | Δ (2θ) |
| [1 1 0] | 13.610 | 6.501 | 100.00 | 13.247 | 6.678 | 100.00 | 0.363 |
| [1 1 1] | 25.589 | 3.478 | 22.57 | 25.111 | 3.544 | 19.89 | 0.478 |
| [-3 -3 1] | 39.681 | 2.270 | 12.17 | 39.057 | 2.304 | 13.61 | 0.624 |
| [-2 -2 1] | 27.511 | 3.240 | 9.85 | 27.303 | 3.264 | 10.85 | 0.208 |
| [-1 1 2] | 33.860 | 2.645 | 9.56 | 34.141 | 2.624 | 7.72 | -0.281 |
| [0 0 2] | 35.677 | 2.515 | 9.05 | 35.678 | 2.515 | 9.02 | -0.001 |
| [-4 -2 1] | 39.255 | 2.293 | 8.22 | 38.117 | 2.359 | 8.83 | 1.138 |
| [2 2 1] | 37.383 | 2.404 | 6.31 | 36.421 | 2.465 | 5.81 | 0.962 |
| [2 2 0] | 27.417 | 3.251 | 6.24 | 26.676 | 3.339 | 7.89 | 0.741 |
|]3 3 1] | 50.868 | 1.794 | 4.95 | 49.410 | 1.843 | 5.84 | 1.458 |
| [1 1 2] | 42.433 | 2.129 | 4.23 | 41.949 | 2.152 | 4.42 | 0.484 |
| [2 0 0] | 18.723 | 4.736 | 4.19 | 17.812 | 4.976 | 3.45 | 0.911 |
| [-3 -1 1] | 27.326 | 3.261 | 3.23 | 26.679 | 3.339 | 3.30 | 0.647 |
| [-5 -3 1] | 52.836 | 1.731 | 3.21 | 51.190 | 1.783 | 3.09 | 1.646 |
| [-4 2 3] | 54.294 | 1.688 | 2.81 | 54.604 | 1.679 | 2.53 | -0.310 |
| [-3 3 3] | 57.809 | 1.594 | 2.77 | 58.195 | 1.584 | 2.75 | -0.386 |
| [-2 0 2] | 31.600 | 2.829 | 2.65 | 31.973 | 2.797 | 1.87 | -0.373 |
| [2 0 2] | 48.159 | 1.888 | 2.39 | 47.121 | 1.927 | 2.31 | 1.038 |
| [-1 3 1] | 33.975 | 2.637 | 2.26 | 33.857 | 2.646 | 2.39 | 0.118 |
| [-5 3 3] | 62.641 | 1.482 | 2.26 | 62.537 | 1.484 | 1.86 | 0.104 |
| [0 2 1] | 26.661 | 3.341 | 2.17 | 26.547 | 3.355 | 1.29 | 0.114 |

Figure S3. Elastic properties of copper squarate as a function of the orientation of the applied pressure: (A) Compressibility; (B) Young modulus; (C) Maximum shear modulus; (D) Surfaces of maximum (green) and minimum Poisson's ratio (red). Red and green colours are employed to distinguish negative and positive property values.

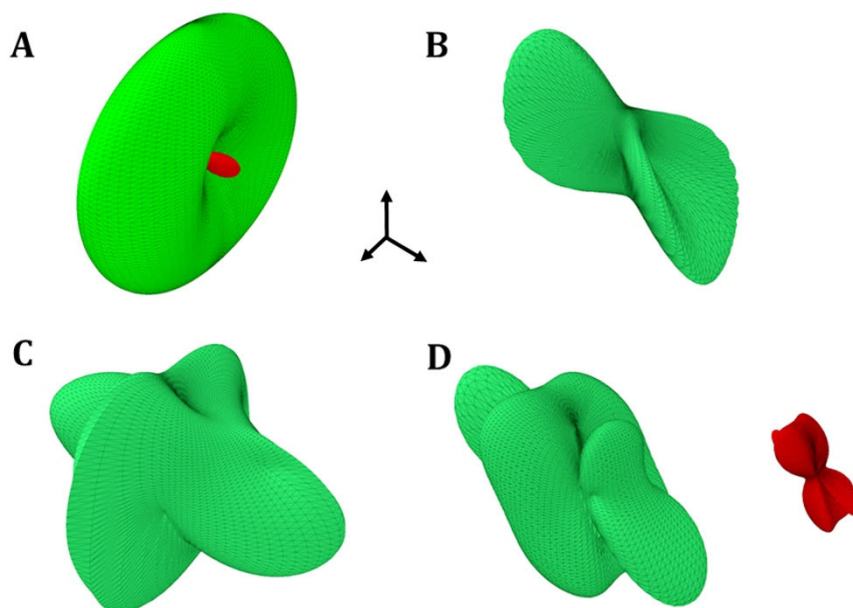


Table S4. Unit cell volume and lattice parameters of copper squarate under the effect of different external isotropic pressures.

| P (GPa) | Vol. (Å ³) | <i>a</i> (Å) | <i>b</i> (Å) | <i>c</i> (Å) | <i>α</i> (deg) | <i>β</i> (deg) | <i>γ</i> (deg) |
|---------|------------------------|--------------|--------------|--------------|----------------|----------------|----------------|
| -1.5001 | 562.4353 | 10.7189 | 9.6763 | 5.9286 | 90.00 | 113.84 | 90.00 |
| -1.2498 | 545.5326 | 10.7991 | 9.5624 | 5.8344 | 90.00 | 115.11 | 90.00 |
| -1.0009 | 535.8749 | 10.8442 | 9.4861 | 5.7779 | 90.00 | 115.63 | 90.00 |
| -0.7497 | 526.9435 | 10.8919 | 9.3978 | 5.7339 | 90.00 | 116.13 | 90.00 |
| -0.4993 | 520.1234 | 10.9398 | 9.3037 | 5.6928 | 90.00 | 116.15 | 90.00 |
| -0.2508 | 512.9415 | 10.9817 | 9.2187 | 5.6540 | 90.00 | 116.35 | 90.00 |
| -0.1243 | 507.1767 | 11.0353 | 9.1237 | 5.6269 | 90.00 | 116.46 | 90.00 |
| 0.0004 | 502.6355 | 11.0961 | 9.0074 | 5.6076 | 90.00 | 116.26 | 90.00 |
| 0.2493 | 497.6242 | 11.1297 | 8.9240 | 5.5811 | 90.00 | 116.14 | 90.00 |
| 0.5005 | 492.9396 | 11.1581 | 8.8690 | 5.5516 | 90.00 | 116.20 | 90.00 |
| 0.7503 | 488.3490 | 11.1865 | 8.7918 | 5.5270 | 90.00 | 116.05 | 90.00 |
| 1.0002 | 483.0001 | 11.2420 | 8.6687 | 5.4985 | 90.00 | 115.66 | 90.00 |
| 1.2507 | 468.0708 | 11.4581 | 8.2106 | 5.4560 | 90.00 | 114.23 | 90.00 |
| 1.5011 | 449.3288 | 11.6623 | 7.7077 | 5.4171 | 90.00 | 112.67 | 90.00 |
| 1.7482 | 427.0266 | 11.8435 | 7.1757 | 5.3910 | 90.00 | 111.24 | 90.00 |
| 2.0006 | 407.6974 | 11.9506 | 6.7755 | 5.3714 | 90.00 | 110.38 | 90.00 |
| 2.4994 | 399.3546 | 11.9715 | 6.6291 | 5.3557 | 90.00 | 110.02 | 90.00 |
| 3.0003 | 388.4434 | 11.9998 | 6.4473 | 5.3346 | 90.00 | 109.75 | 90.00 |
| 4.0004 | 376.5658 | 12.0362 | 6.3041 | 5.2732 | 90.00 | 109.76 | 90.00 |
| 4.9994 | 367.7653 | 12.0196 | 6.1785 | 5.2530 | 90.00 | 109.48 | 90.00 |
| 5.9996 | 361.3961 | 12.0091 | 6.0950 | 5.2309 | 90.00 | 109.28 | 90.00 |

Table S5. Calculated compressibilities ($k_a = -1/a \cdot (\partial a / \partial P)_P$) of copper squarate for different external isotropic pressures.

| P (GPa) | $k_a(\text{TPa}^{-1})$ | P (GPa) | $k_a(\text{TPa}^{-1})$ | P (GPa) | $k_a(\text{TPa}^{-1})$ |
|---------|------------------------|---------|------------------------|---------|------------------------|
| -1.20 | -14.45 | 0.30 | -12.09 | 1.80 | -35.49 |
| -1.10 | -16.29 | 0.40 | -12.91 | 1.90 | -29.64 |
| -1.00 | -18.66 | 0.50 | -10.82 | 2.00 | -16.26 |
| -0.90 | -19.61 | 0.60 | -7.59 | 2.10 | -7.60 |
| -0.80 | -18.70 | 0.70 | -6.45 | 2.20 | -3.37 |
| -0.70 | -16.54 | 0.80 | -10.88 | 2.40 | -4.19 |
| -0.60 | -14.41 | 0.90 | -23.34 | 2.60 | -4.65 |
| -0.50 | -13.85 | 1.00 | -44.10 | 2.80 | -4.79 |
| -0.40 | -16.18 | 1.10 | -62.48 | 3.00 | -4.64 |
| -0.30 | -22.20 | 1.20 | -74.16 | 3.20 | -4.22 |
| -0.20 | -31.66 | 1.30 | -80.56 | 3.40 | -3.58 |
| -0.10 | -42.96 | 1.40 | -80.47 | 3.60 | -2.76 |
| 0.00 | -21.53 | 1.50 | -73.79 | 3.80 | -1.82 |
| 0.10 | -9.07 | 1.60 | -61.79 | 4.00 | -0.81 |
| 0.20 | -9.22 | 1.70 | -47.40 | 4.20 | 0.20 |

Figure S4. Lattice enthalpy of copper squarate as a function of the isotropic pressure.

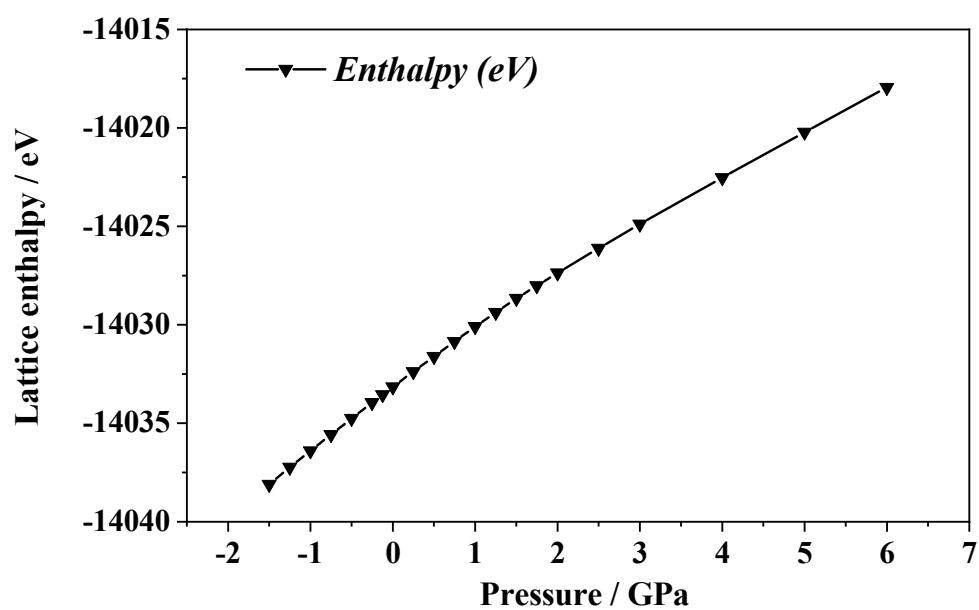


Table S6. Unit cell volume and lattice parameters of copper squarate under the effect of different external uniaxial stresses applied along the direction of minimum compressibility.

| P (GPa) | Vol. (Å³) | a (Å) | b (Å) | c (Å) | α (deg) | β (deg) | γ(deg) |
|----------------|-----------------------------|--------------|--------------|--------------|----------------------------------|---------------------------------|---------------------------------|
| -0.3337 | 494.9934 | 11.5290 | 8.3901 | 5.5363 | 89.61 | 112.43 | 90.09 |
| -0.2490 | 496.9889 | 11.4381 | 8.5302 | 5.5466 | 89.59 | 113.31 | 90.10 |
| -0.1664 | 498.5299 | 11.3440 | 8.6679 | 5.5591 | 89.64 | 114.21 | 90.11 |
| -0.0830 | 499.5203 | 11.2490 | 8.7977 | 5.5751 | 89.72 | 115.13 | 90.10 |
| 0.0007 | 501.3811 | 11.1228 | 8.9756 | 5.6023 | 89.80 | 116.30 | 90.07 |
| 0.0836 | 504.6081 | 10.9101 | 9.2829 | 5.6382 | 89.80 | 117.91 | 90.09 |
| 0.1240 | 506.1968 | 10.8064 | 9.4183 | 5.6653 | 89.83 | 118.61 | 90.08 |
| 0.1656 | 507.5263 | 10.6219 | 9.6598 | 5.7034 | 89.92 | 119.86 | 90.07 |
| 0.1900 | 506.8629 | 10.5947 | 9.6910 | 5.7109 | 89.92 | 120.18 | 90.07 |
| 0.2079 | 504.8509 | 10.5625 | 9.7158 | 5.7203 | 89.93 | 120.68 | 90.07 |
| 0.2496 | 503.0695 | 10.4704 | 9.8136 | 5.7458 | 89.87 | 121.56 | 90.05 |

Table S7. Calculated volumetric compressibilities ($k_V = -1/V \cdot (\partial V/\partial P)_P$) of copper squarate for different external uniaxial stresses applied along the the direction of minimum compressibility.

| P (GPa) | $k_V(\text{TPa}^{-1})$ | P (GPa) | $k_V(\text{TPa}^{-1})$ |
|---------|------------------------|---------|------------------------|
| -0.30 | -50.38 | 0.08 | -75.98 |
| -0.27 | -55.53 | 0.09 | -77.57 |
| -0.24 | -49.01 | 0.10 | -79.49 |
| -0.21 | -38.20 | 0.11 | -81.06 |
| -0.18 | -28.23 | 0.12 | -81.28 |
| -0.15 | -22.25 | 0.13 | -78.74 |
| -0.12 | -21.78 | 0.14 | -71.63 |
| -0.09 | -26.95 | 0.15 | -57.66 |
| -0.06 | -36.82 | 0.16 | -34.02 |
| -0.03 | -49.61 | 0.17 | 2.65 |
| 0.00 | -63.04 | 0.18 | 56.36 |
| 0.03 | -74.58 | 0.19 | 131.85 |
| 0.06 | -75.07 | 0.20 | 234.70 |
| 0.07 | -75.11 | - | - |

Reference

1. Dinnebier R.E.; Nuss H.; Jansen, M. Anhydrous CuC_4O_4 , a Channel Structure solved from X-ray Powder Diffraction Data. *Z. Anorg. Allg. Chem.* **2005**, 63, 2328–2332.