**Table S1.** Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$ ) for $[Cu(iz)_2(can)_2]$ from multipole refinement.U(eq) is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| $Cu^{2+}$(1) | 0.50000 | 0.00000 | 0.5000 | 0.009 |
| O(11) | 0.31779(6) | 0.52337(3) | 0.65234(8) | 0.016 |
| O(12) | 0.09841(7) | 0.61726(4) | 0.74348(9) | 0.024 |
| N(2) | 0.40935(6) | 0.36349(3) | 0.00133(4) | 0.011 |
| N(5) | 0.22114(7) | 0.23782(4) | 0.02532(4) | 0.015 |
| N(7) | 0.29967(6) | 0.54052(3) | 0.16918(7) | 0.013 |
| N(9) | 0.11689(5) | 0.60673(3) | 0.42461(7) | 0.014 |
| N(10) | 0.18172(5) | 0.58058(3) | 0.61467(6) | 0.012 |
| C(3) | 0.51005(6) | 0.27798(3) | -0.01756(5) | 0.013 |
| C(4) | 0.39368(7) | 0.19927(3) | -0.00279(5) | 0.014 |
| C(6) | 0.23547(6) | 0.33623(3) | 0.02686(5) | 0.014 |
| C(8) | 0.21996(5) | 0.56851(3) | 0.29626(6) | 0.011 |

**Table S2.** Anisotropic displacement parameters ($Å^2$ ) for $[Cu(iz)_2(can)_2]$. The anisotropic displacement factor exponent takes the form:

$$-2\pi^2 [ h^2 a^{*2} U11 + ... + 2 h k a^* b^* U_{12} ] .$$

| | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| $Cu^{2+}$(1) | 0.01002(3) | 0.00745(4) | 0.00898(3) | -0.00065(3) | 0.00431(3) | -0.00057(3) |
| O(11) | 0.0163(1) | 0.0181(1) | 0.0132(2) | 0.0063(1) | 0.0011(1) | 0.0011(1) |
| O(12) | 0.0223(2) | 0.0369(2) | 0.0128(2) | 0.0121(2) | 0.0071(1) | -0.0018(1) |
| N(2) | 0.0115(1) | 0.0083(1) | 0.0121(1) | -0.0014(1) | 0.0043(1) | -0.0004(1) |
| N(5) | 0.0157(2) | 0.0132(2) | 0.0155(2) | -0.0062(1) | 0.0038(1) | -0.0012(1) |
| N(7) | 0.0134(1) | 0.0128(1) | 0.0126(1) | 0.0007(1) | 0.0064(1) | -0.0014(1) |
| N(9) | 0.0135(1) | 0.0181(1) | 0.0108(1) | 0.0064(1) | 0.0038(1) | 0.0003(1) |
| N(10) | 0.0114(1) | 0.0155(1) | 0.0099(1) | 0.0029(1) | 0.0034(1) | 0.0000(1) |
| C(3) | 0.0136(1) | 0.0094(1) | 0.0148(2) | 0.0000(1) | 0.0036(1) | 0.0009(1) |
| C(4) | 0.0184(2) | 0.0093(1) | 0.0152(2) | -0.0022(1) | 0.0023(1) | 0.0005(1) |
| C(6) | 0.0120(1) | 0.0126(2) | 0.0161(2) | -0.0028(1) | 0.0050(1) | -0.0019(1) |
| C(8) | 0.0112(1) | 0.0119(1) | 0.0105(1) | 0.0009(1) | 0.0041(1) | -0.0007(1) |

**Table S3.** Hydrogen coordinates and isotropic displacement parameters [Å$^2$] for $[Cu(iz)_2(can)_2]$.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(3) | 0.65739(6) | 0.27985(3) | -0.03922(5) | 0.037(2) |
| H(4) | 0.41587(7) | -0.12095(3) | -0.01238(5) | 0.038(2) |
| H(5) | 0.10018(7) | 0.20246(4) | 0.04406(4) | 0.029(3) |
| H(6) | 0.11944(6) | 0.38507(3) | 0.04465(5) | 0.036(2) |

**Table S4.** Bond lengths [Å] and angles [deg] for $[Cu(iz)_2(can)_2]$.

| | | | |
|---|---|---|---|
| CU2+(1)-O(11)$^{i}$ | 2.5566(5) | N(5) - C(6) | 1.3423(6) |
| CU2+(1)-N(2) | 1.9660(4) | N(7) - C(8) | 1.1607(6) |
| CU2+(1)-N(7) | 2.0273(5) | N(9) - N(10) | 1.3589(6) |
| O(11) - N(10) | 1.2422(6) | N(9) - C(4) | 1.3719(6) |
| O(12) - N(10) | 1.2285(6) | N(9) - C(8) | 1.3210(6) |
| O(12) - C(4) | 1.9871(7) | N(10) - H(4) | 1.0661(6) |
| O(12) - H(4) | 1.5611(7) | C(3) - C(4) | 1.3662(6) |
| N(2) - C(3) | 1.3816(5) | C(3) - H(3) | 1.08000(1) |
| N(2) - C(6) | 1.3271(5) | C(4) - H(4) | 1.08000(2) |
| N(5) - C(4) | 1.3736(7) | C(6) - H(6) | 1.08001(2) |
| N(5) - H(5) | 1.01001(1) | C(8) - H(4) | 1.9975(6) |

| D—H••••A | D—H | H••••A | D••••A | D—H••••A |
|---|---|---|---|---|
| C6—H6••••N7 | 1.080(1) | 2.557(1) | 2.957(2) | 100.9(1) |
| C3—H3••••N7$^{iii}$ | 1.080 (1) | 2.630(1) | 3.063(1) | 103.2(1) |
| C4—H4••••O11$^{iv}$ | 1.080 (1) | 2.411(1) | 3.276(2) | 136.1(1) |
| C4—H4••••O11$^{v}$ | 1.080 (1) | 2.601(1) | 3.400(1) | 130.2(1) |
| N5—H5••••O12$^{vi}$ | 1.010 (1) | 2.532(1) | 3.173(1) | 121.1(1) |
| N5—H5••••N9$^{vi}$ | 1.010 (1) | 2.055(1) | 3.052(1) | 169.1(1) |
| C6—H6••••O12$^{vii}$ | 1.080 (1) | 2.258(1) | 3.085(2) | 131.8(1) |

| | | | |
|---|---|---|---|
| N(2) - CU2+(1) - N(2)$^{i}$ | 180.0 | O(11) - N(10) - N(9) | 121.0(1) |
| N(2) - CU2+(1) - N(7) | 89.8(1) | O(12) - N(10) - N(9) | 115.9(1) |
| N(2) - CU2+(1) - O(11) | 89.8(1) | N(2) - C(3) - C(4) | 109.0(1) |
| N(7) - CU2+(1) - O(11) | 100.5(1) | N(2) - C(3) - H(3) | 121.3(1) |
| O(11)$^{i}$ - CU2+(1) - O(11)$^{ii}$ | 180.0 | C(4) - C(3) - H(3) | 129.7(1) |
| CU2+(1) - N(2) - C(3) | 128.3(1) | N(5) - C(4) - C(3) | 105.9(1) |
| CU2+(1) - N(2) - C(6) | 125.3(1) | N(5) - C(4) - H(4) | 121.7(1) |
| C(3) - N(2) - C(6) | 106.4(1) | C(3) - C(4) - H(4) | 132.3(1) |
| C(4) - N(5) - C(6) | 108.3(1) | N(2) - C(6) - N(5) | 110.4(1) |
| CU2+(1) - N(7) - C(8) | 164.8(1) | N(2) - C(6) - H(6) | 125.8(1) |
| N(10) - N(9) - C(8) | 112.2(1) | N(5) - C(6) - H(6) | 123.8(1) |
| O(11) - N(10) - O(12) | 123.1(1) | N(7) - C(8) - N(9) | 173.2(1) |

Symmetry transformations used to generate equivalent atoms:

i) x, y, z-1; ii) x, y, 1+z; iii) 1-x, 1-y, -z; iv) x, 1/2-y, -1/2+z; v) 1-x, -1/2+y, 1/2-z;

vi) -x, -1/2+y, 1/2-z; vii) -x, 1-y, 1-z

**Table S5.** Population parameters for copper and oxygen atoms.

| **Atom** | **Cu+2(1)** | **O(11)** | **O(12)** |
|---|---|---|---|
| $\kappa$ | 0.975(3) | 0.990(2) | 0.990(2) |
| $\kappa'$ | 0.990(3) | 1.000 | 1.000 |
| $P_{val}$ | 4.523(18) | 6.089(20) | 6.106(20) |
| $P_{11+}$ | - | -0.040(11) | -0.079(12) |
| $P_{11-}$ | - | -0.010(9) | 0.027(10) |
| $P_{20}$ | 0.027(8) | 0.007(11) | -0.044(14) |
| $P_{22+}$ | -0.006(7) | -0.105(11) | -0.121(12) |
| $P_{22-}$ | 0.014(7) | -0.015(10) | -0.028(11) |
| $P_{31+}$ | - | 0.003(8) | -0.009(9) |
| $P_{31-}$ | - | 0.004(8) | 0.047(9) |
| $P_{33+}$ | - | 0.019(8) | 0.027(8) |
| $P_{33-}$ | - | 0.011(8) | -0.011(8) |
| $P_{40}$ | -0.027(8) | - | - |
| $P_{42+}$ | 0.007(8) | - | - |
| $P_{42-}$ | -0.008(8) | - | - |
| $P_{44+}$ | -0.099(7) | - | - |
| $P_{44-}$ | -0.007(7) | - | - |

**Table S6.** Population parameters for nitrogen atoms.

| **Atom** | **N(2)** | **N(5)** | **N(7)** | **N(9)** | **N(10)** |
|---|---|---|---|---|---|
| $\kappa$ | 0.976(2) | 1.062(2) | 0.976(2) | 0.998(3) | 1.005(4) |
| $\kappa'$ | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 |
| $P_{val}$ | 5.263(26) | 4.991(55) | 5.424(31) | 5.179(32) | 4.694(39) |
| $P_{11+}$ | -0.064(9) | -0.004(11) | -0.010(14) | -0.082(10) | 0.027(10) |
| $P_{11-}$ | -0.070(9) | -0.015(12) | -0.000(10) | -0.090(10) | -0.034(10) |
| $P_{20}$ | -0.141(9) | -0.111(12) | -0.054(10) | 0.030(10) | -0.183(11) |
| $P_{22+}$ | -0.033(10) | -0.009(12) | 0.224(11) | -0.082(11) | 0.021(11) |
| $P_{22-}$ | 0.068(9) | 0.047(11) | -0.054(10) | 0.001(10) | 0.040(11) |
| $P_{31+}$ | -0.020(8) | 0.013(9) | -0.008(9) | -0.036(9) | -0.004(9) |
| $P_{31-}$ | -0.009(8) | 0.013(9) | -0.000(8) | -0.016(9) | 0.018(8) |
| $P_{33+}$ | 0.158(9) | 0.162(11) | 0.024(9) | 0.144(9) | 0.284(12) |
| $P_{33-}$ | -0.074(9) | -0.098(10) | 0.021(9) | -0.021(9) | -0.028(11) |

**Table S7.** Population parameters for carbon atoms.

| Atom | C(3) | C(4) | C(6) | C(8) |
|---|---|---|---|---|
| $\kappa$ | 1.015(4) | 1.015(4) | 1.015(4) | 1.049(5) |
| $\kappa'$ | 1.000 | 1.000 | 1.000 | 1.000 |
| $P_{val}$ | 3.898(32) | 3.916(34) | 3.934(37) | 3.655(41) |
| $P_{11+}$ | 0.077(12) | -0.013(13) | -0.010(12) | -0.076(18) |
| $P_{11-}$ | -0.021(11) | 0.023(13) | -0.029(12) | 0.003(10) |
| $P_{20}$ | -0.177(11) | -0.172(11) | -0.225(11) | -0.134(11) |
| $P_{22+}$ | 0.027(11) | -0.040(14) | 0.021(12) | 0.286(15) |
| $P_{22-}$ | 0.042(11) | 0.003(12) | 0.018(12) | 0.071(11) |
| $P_{31+}$ | 0.003(10) | -0.030(11) | -0.003(10) | -0.021(12) |
| $P_{31-}$ | -0.018(10) | 0.040(10) | -0.009(10) | 0.007(9) |
| $P_{33+}$ | 0.285(12) | 0.223(13) | 0.287(13) | 0.097(13) |
| $P_{33-}$ | -0.088(11) | -0.092(12) | -0.086(12) | 0.039(13) |

**Table S8.** Population parameters for hydrogen atoms.

| **Atom** | **H(3)** | **H(4)** | **H(5)** | **H(6)** |
|---|---|---|---|---|
| $\kappa$ | 1.062(21) | 1.062(21) | 1.062(21) | 1.062(21) |
| $\kappa'$ | 1.000 | 1.000 | 1.000 | 1.000 |
| $P_{val}$ | 0.997(24) | 0.997(24) | 0.838(30) | 0.997(24) |
| $P_{10}$ | 0.141(9) | 0.141(9) | 0.122(15) | 0.141(9) |

**Table S9.** The measured and optimized distances for faces of the crystal.

| No. | {hkl} | Measured distance [mm] | Optimized distance [mm] |
|---|---|---|---|
| 1 | {1 0 0} | 0.198 | 0.19456 |
| 2 | {-1 0 0} | 0.229 | 0.21644 |
| 3 | {0 1 0} | 0.118 | 0.12697 |
| 4 | {0 -1 0} | 0.114 | 0.10503 |
| 5 | {0 2 -1} | 0.266 | 0.27001 |
| 6 | {0 -2 1} | 0.305 | 0.31999 |
| 7 | {1 -2 0} | 0.171 | 0.17325 |
| 8 | {-1 2 0} | 0.171 | 0.16875 |
| 9 | {1 -1 -1} | 0.213 | 0.22837 |
| 10 | {-1 1 1} | 0.168 | 0.18163 |
| 11 | {1 1 -1} | 0.208 | 0.18282 |
| 12 | {-1 -1 1} | 0.194 | 0.21818 |
| 13 | {0 -1 -1} | 0.299 | 0.34023 |
| 14 | {0 1 1} | 0.284 | 0.31477 |
| 15 | {1 2 0} | 0.181 | 0.19018 |
| 16 | {-1 -1 0} | 0.202 | 0.18672 |
| 17 | {1 1 1} | 0.303 | 0.33345 |