

SUPPORTING INFORMATION

Modeling triple conformational disorder in a new crystal polymorph of *cis* aquabis(L-isoleucinato)copper(II)

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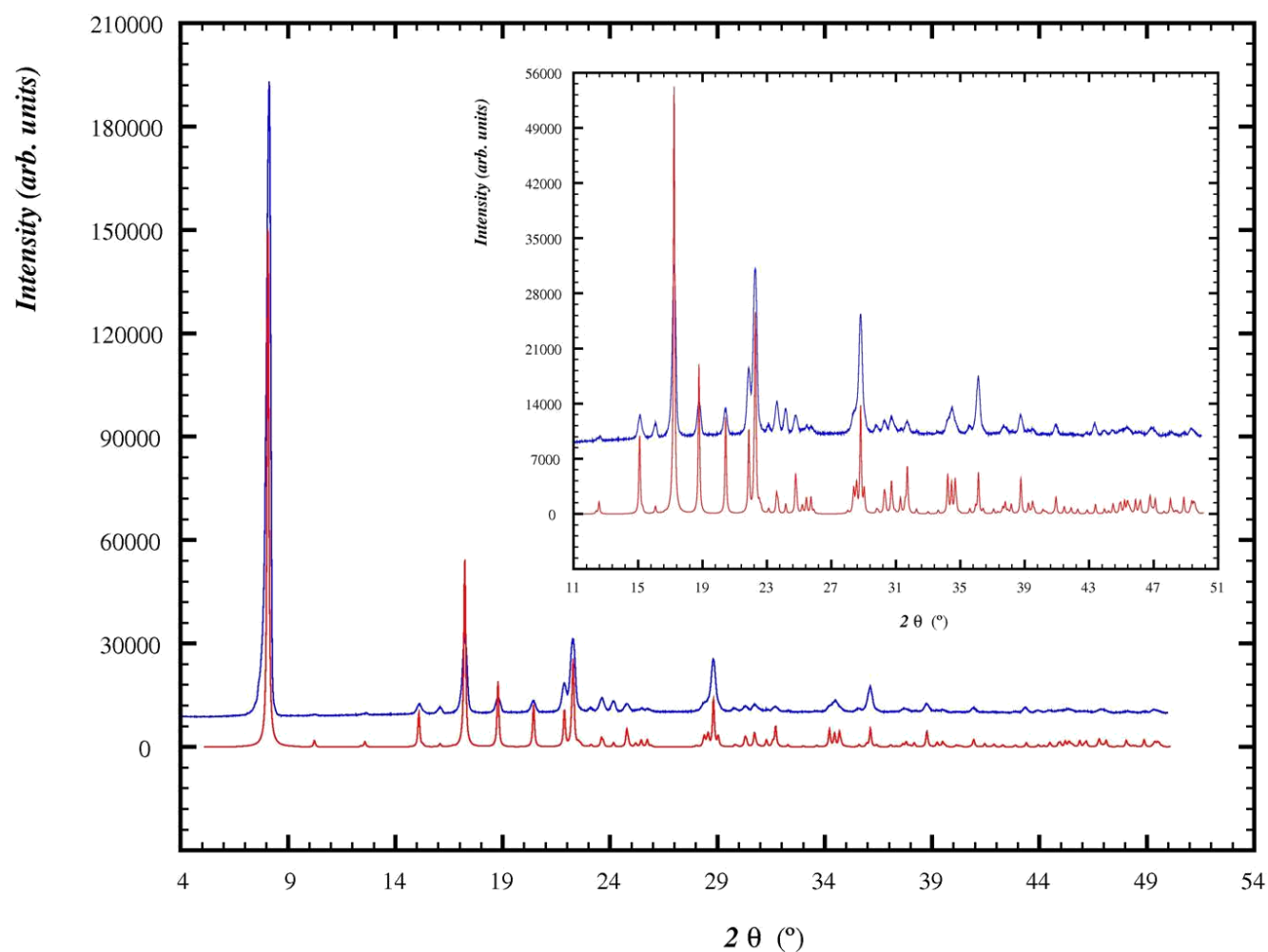


Figure S1. Comparison of simulated (red) and experimental PXRD patterns (blue) of the monoclinic polymorph of *cis* Cu(L-Ile)₂·H₂O (**2**) (sample A). Magnified patterns for 2θ -range 11–50° are shown in the insert. The experimental pattern indicates preferred orientation of crystallites due to their plate-like shape. The simulated PXRD pattern of **2** was calculated using Mercury.¹ The figure was made using WinPLOTR,² a part of FullProf Suite.³

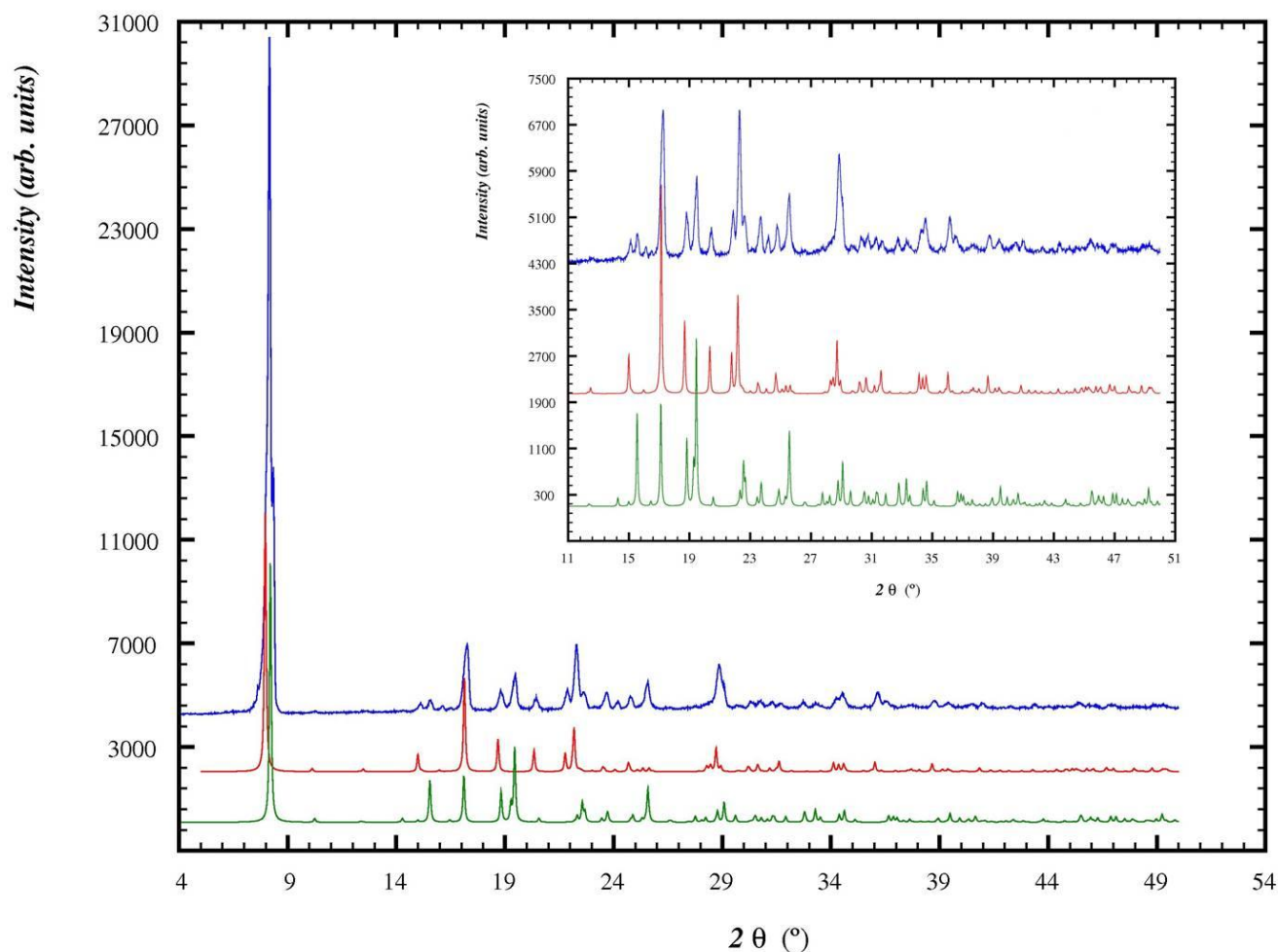


Figure S2. Experimental PXRD pattern (blue) of the *cis* Cu(L-Ile)₂·H₂O sample B obtained after the recrystallization from acetic acid–water mixture compared with the simulated patterns for polymorphs **1** (green) and **2** (red). Magnified patterns for 2θ-range 11–50° are shown in the insert. The *cis* Cu(L-Ile)₂·H₂O sample in this case is a mixture of both polymorphs. The PXRD patterns of **1** and **2** were simulated using Mercury.¹ The figure was made using WinPLOTR,² a part of FullProf Suite.³

References:

1. Macrae, C. F.; Bruno, I. J.; Chisholm, J. A.; Edgington, P. R.; McCabe, P.; Pidcock, E.; Rodriguez-Monge, L.; Taylor, R.; van de Streek, J.; Wood, P. A. *J. Appl. Crystallogr.* **2008**, *41*, 466–470.
2. Roisnel, T.; Rodriguez-Carvajal, J. WinPLOTR: a Windows tool for powder diffraction patterns analysis. In *Materials Science Forum, Proceedings of the Seventh European Powder Diffraction Conference (EPDIC 7) 2000*; Delhez R. and E.J. Mittenmeijer E. J., Eds., **2000**, pp 118–123.
3. Rodriguez-Carvajal, J. *Physica B* **1993**, *192*, 55–69.

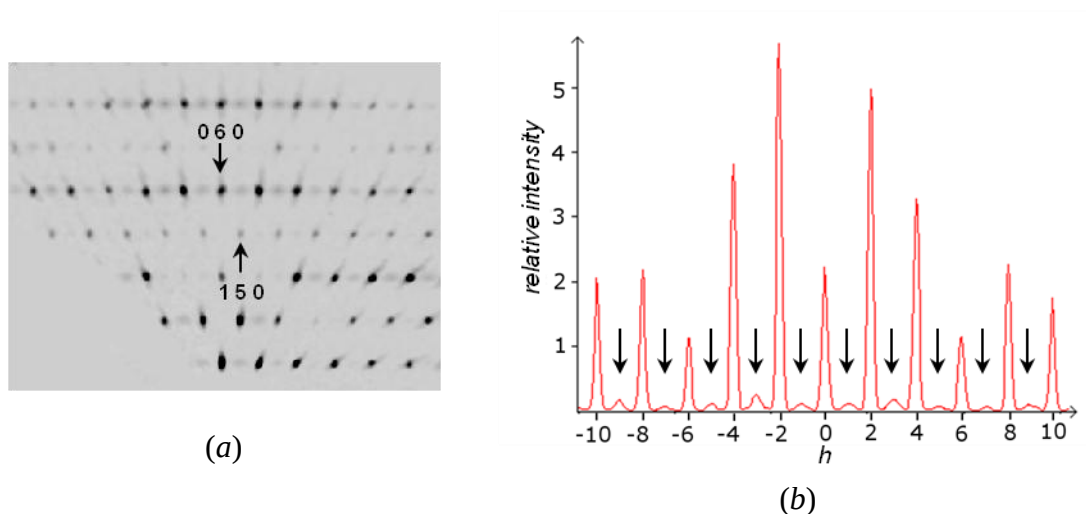


Figure S3. Due to the disorder in the crystal structure of the *C2* polymorph, diffuse scattering streaks occur in addition to the discrete diffraction maxima: (a) a detail of the reconstructed precession image of *hk0* reciprocal layer for **3**; (b) intensity profile *h60* extracted from the *hk0* reciprocal layer for **3**. Arrows in (b) point to small maxima of diffuse scattering observed for *h* odd.

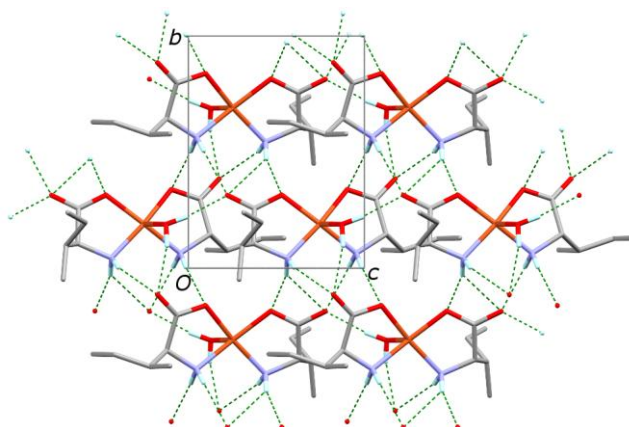


Figure S4. Hydrogen bonding network (shown as green dashed lines) in **3** joins the molecules in a layer parallel to the crystallographic *bc*-plane. Only the major conformer *ce1-ca6* is shown. Carbon-bonded hydrogen atoms are omitted for clarity.

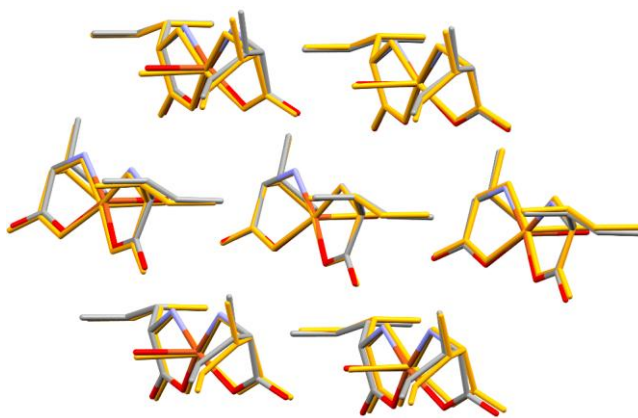


Figure S5. Structure of molecular layers formed by hydrogen bonding is the same for both $P2_12_12_1$ (**1**, shown in orange) and $C2$ (**3**, only the major conformer ce1-ca6 is shown) polymorphs of *cis* Cu(L-Ile)₂·H₂O. Hydrogen atoms are omitted for clarity.

Table S1. Hydrogen bonding in **1**, **2** and **3**

D–H···A	$d(\text{D–H})/\text{\AA}$	$d(\text{H···A})/\text{\AA}$	$d(\text{D···A})/\text{\AA}$	$\angle(\text{D–H···A})^\circ$	Symmetry operator on A
1					
N1–H1A···O11	0.92	2.20	3.085(1)	161	$2 - x, \frac{1}{2} + y, \frac{1}{2} - z$
N1–H1B···O22	0.92	2.07	2.861(1)	143	$1 - x, \frac{1}{2} + y, \frac{1}{2} - z$
O1W–H1W···O22	0.88(2)	1.92(2)	2.786(1)	168(2)	$1 + x, y, z$
N2–H2A···O21	0.92	2.13	3.019(1)	162	$1 - x, \frac{1}{2} + y, \frac{1}{2} - z$
N2–H2B···O12	0.92	2.22	2.989(1)	141	$2 - x, \frac{1}{2} + y, \frac{1}{2} - z$
O1W–H2W···O12	0.77(2)	2.15(2)	2.904(1)	164(2)	$2 - x, \frac{1}{2} + y, \frac{1}{2} - z$
2					
N1–H1A···O11	0.90	2.27	3.138(4)	162	$\frac{1}{2} - x, y - \frac{1}{2}, 2 - z$
N1–H1B···O22	0.90	2.12	2.884(4)	142	$\frac{1}{2} - x, y - \frac{1}{2}, 1 - z$
O1W–H1W···O22	0.89(2)	1.90(2)	2.782(3)	177(1)	$x, y, 1 + z$
N2–H2A···O21	0.90	2.13	3.016(4)	167	$\frac{1}{2} - x, y - \frac{1}{2}, 1 - z$
N2–H2B···O12	0.90	2.26	3.031(3)	144	$\frac{1}{2} - x, y - \frac{1}{2}, 2 - z$
O1W–H2W···O12	0.89(2)	2.11(2)	2.884(5)	146(3)	$\frac{1}{2} - x, y - \frac{1}{2}, 2 - z$
3					
N1–H1A···O11	0.92	2.18	3.078(3)	165	$\frac{1}{2} - x, y - \frac{1}{2}, 2 - z$
N1–H1B···O22	0.92	2.09	2.844(3)	138	$\frac{1}{2} - x, y - \frac{1}{2}, 1 - z$
O1W–H1W···O22	0.89(1)	1.88(1)	2.766(2)	170(2)	$x, y, 1 + z$
N2–H2A···O21	0.92	2.11	3.009(3)	164	$\frac{1}{2} - x, y - \frac{1}{2}, 1 - z$
N2–H2B···O12	0.92	2.20	2.996(2)	144	$\frac{1}{2} - x, y - \frac{1}{2}, 2 - z$
O1W–H2W···O12	0.89(1)	2.04(1)	2.890(3)	160(3)	$\frac{1}{2} - x, y - \frac{1}{2}, 2 - z$

The Conformational (Strain) Potential Energy

The conformational (strain) potential energy of a molecule was calculated from the following basic formula:

$$\begin{aligned}
 V_{\text{strain}} &= V(b) + V(\theta) + V(\varphi) + V(\chi) + V_{\text{LJ}} + V_{\text{Coulomb}} = \\
 &= \sum_{\text{bonds}} D_e (e^{-2\alpha(b-b_0)} - 2e^{-\alpha(b-b_0)} + 1) + \frac{1}{2} \sum_{\substack{\text{valence} \\ \text{angles}}} k_\theta (\theta - \theta_0)^2 + \\
 &+ \frac{1}{2} \sum_{\substack{\text{torsion} \\ \text{angles}}} V_\varphi (1 \pm \cos n\varphi) + \frac{1}{2} \sum_{\substack{\text{out-of-plane} \\ \text{angles}}} k_\chi \chi^2 + \sum_{i < j} (A_i A_j r_{ij}^{-12} - B_i B_j r_{ij}^{-6}) + \sum_{l < m} q_l q_m r_{lm}^{-1}
 \end{aligned} \tag{1}$$

Here b , θ , φ , χ and r are the bond length; the valence, torsion, and out-of-plane angles, and the nonbonded distance, respectively. D_e , α , b_0 , k_θ , θ_0 , k_χ , V_φ and n are the empirical parameters. A and B are one-atom empirical parameters of the Lennard-Jones 12–6 function, V_{LJ} . The q is an empirical parameter for atomic partial charge. The intramolecular nonbonded interactions were calculated between the atoms separated by three or more bonds by the V_{LJ} and electrostatic, $V_{\text{Coulomb,NB}}$, potentials. The electrostatic potential was also applied to model the 1,3 repulsive interactions between the two amino nitrogen and two carboxylato oxygen atoms coordinated to the copper(II), $V_{\text{Coulomb,1-3}}$.

Table S2. MD average values of energy contributions and corresponding rms deviations calculated from the values attained during 20 ns of MD simulations at room temperature for ta9-ta9 conformer of the Cu(L-Ile)₂·3435H₂O system^{a,b}

	Energy (kJ mol ⁻¹)	
	average value	rms
Potential energy	-161902.0	306.9
Kinetic energy	25992.7	185.9
Total energy	-135910.0	245.2
Cu(L-Ile) ₂ Intramolecular Contributions		
$V(b)$	52.2	11.0
$V(\theta)$	72.7	12.1
$V(\varphi)$	72.6	9.1
$V(\chi)$	4.6	2.4
$V_{Coulomb,1-3}$	2304.6	26.4
$V_{Coulomb,NB}$	-1727.3	25.8
V_{LJ}	101.9	10.6
V_{strain}	881.3	
Intermolecular Interactions between Cu(L-Ile) ₂ and Water Molecules		
$V_{Coulomb,SR}$	-411.6	46.2
$V_{Coulomb,LR}$	-53.1	36.1
$V_{LJ,SR}$	-103.6	16.3
$V_{LJ,LR}$	-9.2	0.3
Intermolecular Interactions between the Water Molecules		
$V_{Coulomb,SR}$	-188268.0	514.8
$V_{Coulomb,LR}$	-4587.9	260.5
$V_{LJ,SR}$	31101.0	323.8
$V_{LJ,LR}$	-451.3	1.4

^a The total energy is the sum of the kinetic and potential energies. The intramolecular contributions to V_{strain} are described in Eq. (1).

^b LR and SR stand for long-range and short-range intermolecular energy contributions, respectively

Table S3. FFWa-SPCE minimum $V_{\text{in-crystal}}$ and $V_{\text{intermolecular}}$ values (kJ mol^{-1}) estimated for anhydrous and aqua $\text{Cu}(\text{L-Ile})_2$ systems in $P2_12_12_1$ and $C2$ unit cell packings for denoted conformers with *cis*- and *trans*-configuration. Empty space means that the corresponding conformer had unfavorable starting packing and thus changed to another conformer via the energy minimization.

conformer	<i>cis</i> $\text{Cu}(\text{L-Ile})_2 \cdot \text{H}_2\text{O}$				<i>trans</i> $\text{Cu}(\text{L-Ile})_2 \cdot \text{H}_2\text{O}$				<i>cis</i> $\text{Cu}(\text{L-Ile})_2$				<i>trans</i> $\text{Cu}(\text{L-Ile})_2$			
	$V_{\text{in-crystal}}$		$V_{\text{intermolecular}}$		$V_{\text{in-crystal}}$		$V_{\text{intermolecular}}$		$V_{\text{in-crystal}}$		$V_{\text{intermolecular}}$		$V_{\text{in-crystal}}$		$V_{\text{intermolecular}}$	
	$P2_12_12_1$	$C2$	$P2_12_12_1$	$C2$	$P2_12_12_1$	$C2$	$P2_12_12_1$	$C2$	$P2_12_12_1$	$C2$	$P2_12_12_1$	$C2$	$P2_12_12_1$	$C2$	$P2_12_12_1$	$C2$
e1-a1	451	461	-469	-460	461	470	-340	-333	499	520	-406	-387	501		-324	
e1-a2	484	504	-470	-454	532	561	-315	-290	538		-406		530	646	-309	-200
e1-a3	449	462	-464	-462	459	479	-343	-329	510		-398			482		-345
e1-a4	463	474	-464	-454	509	510	-343	-347	519	535	-402	-387		572		-285
e1-a5	541	546	-467	-472	557	566	-342	-324					601	603	-312	-286
e1-a6	475	475	-481	-475		482		-359		549		-391		541		-283
e1-a7	461	465	-483	-477	482	482	-363	-350	538	544	-397	-391		534		-304
e1-a8	460	463	-482	-475	477	466	-349	-353	538	538	-400	-400				
e1-a9	452	458	-479	-473	458	455	-346	-352	515		-426		499	509	-314	-289
a1-a1	440	456	-455	-437	497		-296		483	490	-406	-399	576		-214	
a1-a2					480	495	-367	-337						549		-277
a1-a3	436	460	-454	-436	486	496	-313	-310	484	476	-406	-409				
a1-a4	462	462	-458	-457	571		-287		502	502	-411	-412	633		-217	
a1-a5	533	557	-450	-436	599	612	-276	-285		590		-391	649		-223	
a1-a6	468	483	-451	-439	501	534	-342	-290	522	526	-417	-400	583		-264	
a1-a7	459	461	-453	-452	553	573	-270	-240	526	527	-391	-399		596		-210
a1-a8	494	467	-416	-441	529	488	-299	-333	519	501	-394	-419	553	540	-272	-269
a1-a9	449	453	-438	-433	533	522	-327	-273	493	499	-411	-403	579	583	-278	-195

Table S4. FFWa-SPCE in-crystal energy values and unit cell dimensions predicted for asymmetric-unit conformer pairs of *cis* Cu(L-Ile)₂·H₂O, space group *P2*₁

Conformer pair	$V_{\text{in-crystal}}$ (kJ mol ⁻¹)	$V_{\text{intermolecular}}$ (kJ mol ⁻¹)	a (Å)	b (Å)	c (Å)	β (°)	V (Å ³)
ca1-ce1, ce1-ca1	1011.3	-833.2	7.389	10.141	21.823	93.7	1631.8
ce1-ca1, ce1-ca3	903.8	-870.9	8.049	9.268	23.390	100.7	1714.4
ca1-ce1, ce1-ca3	997.2	-834.9	7.427	10.226	21.828	87.1	1655.7
ce1-ca1, ce1-ca8	936.6	-923.2	7.661	9.894	21.996	95.9	1658.3
ce1-ca1, ce1-ca9	902.8	-936.1	7.960	9.327	22.199	96.3	1638.1
ce1-ca3, ce1-ca1	903.6	-930.9	8.050	9.168	23.899	100.8	1714.4
ce1-ca3, ce1-ca6	931.9	-935.9	7.756	9.288	23.055	91.0	1661.0
ce1-ca6, ca1-ca1	943.7	-906.0	7.474	9.573	21.282	93.9	1702.3
ce1-ca8, ce1-ce1	986.7	-881.9	7.226	10.655	21.892	102.9	1643.2
ce1-ca9, ce1-ca1	929.5	-899.7	7.699	9.840	22.721	93.6	1718.1
ce1-ca9, ce1-ca3	888.5	-924.9	7.751	9.336	23.240	95.5	1674.1

Table S5. Selected bond distances (Å) and angles (deg) of *cis* Cu(L-Ile)₂·H₂O in the minimum MM crystal structures with one conformer type in the crystal lattice

Starting X-ray Structure for Geometry Optimization	1	2; 3	2	3	2; 3
Conformer	ce1-ca6	ce1-ca6	ce1-ca9	ce1-ca9	ce1-ca8
<i>Bond distances</i>					
Cu1–N1	1.992	1.994	1.993	1.993	1.993
Cu1–N2	1.993	1.995	1.999	1.996	1.996
Cu1–O11	1.922	1.925	1.927	1.925	1.926
Cu1–O21	1.920	1.923	1.925	1.920	1.924
Cu1–O1W	3.017	2.606	2.426	2.366	2.910
<i>Valence angles</i>					
N1–Cu1–O11	85.6	85.2	85.7	85.2	85.6
N1–Cu1–O21	160.5	149.1	153.7	140.8	158.3
N2–Cu1–O11	163.1	177.0	169.6	170.3	162.6
N2–Cu1–O21	86.7	86.2	85.5	86.3	85.5
N1–Cu1–N2	97.3	95.9	92.2	96.8	96.2
O11–Cu1–O21	85.3	91.3	91.9	86.1	86.5
<i>Torsion angles</i>					
O11–Cu1–N1–C12	15.9	20.8	15.0	20.0	15.1
C13–C12–N1–Cu1	–145.7	–152.7	–143.6	–151.3	–146.0
C14–C13–C12–N1	77.3	76.6	81.2	79.5	78.0
C16–C15–C13–C12	66.9	65.6	73.8	72.6	68.7
O21–Cu1–N2–C22	–5.8	–13.5	–21.8	–12.3	–19.6
C23–C22–N2–Cu1	–113.4	–105.8	–93.4	–103.8	–93.8
C24–C23–C22–N2	–61.8	–60.4	159.9	160.9	168.0
C26–C25–C23–C22	166.8	165.3	166.3	179.2	–49.3