

Molecule vs. Crystal: Polymorphism of the Simple Complex $(^n\text{Bu}_4\text{N})_2[\text{Cu}(\text{orot})_2]\cdot 2\text{H}_2\text{O}$ and Ostwald's Step Rule

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Ostwald's Step Rule (also, Ostwald's Rule of Stages) is invoked to explain the solvent-mediated transformation of crystals of a simple transition-metal complex to a second polymorph that presents a slightly less stable conformation about the metal center.

Copper carbonate, orotic acid and tetra-*n*-butylammonium hydroxide react in water to give $(^n\text{Bu}_4\text{N})_2[\text{Cu}(\text{orot})_2]\cdot 2\text{H}_2\text{O}$ (H_2orot is orotic acid, $\text{C}_5\text{H}_4\text{N}_2\text{O}_4$), which crystallized in space group $P2_1/n$, $V = 4913.2$ (4) \AA^3 , $Z = 4$; it was structurally characterized at room temperature. In this product, **form I, the coordination environment of the Cu center is distorted from planar geometry.**

[$\tau_4 = 0.34$ Yang, L., *et al.* (2007). *Dalton Trans.* 955-964. DOI: 10.1039/b617136b] ①

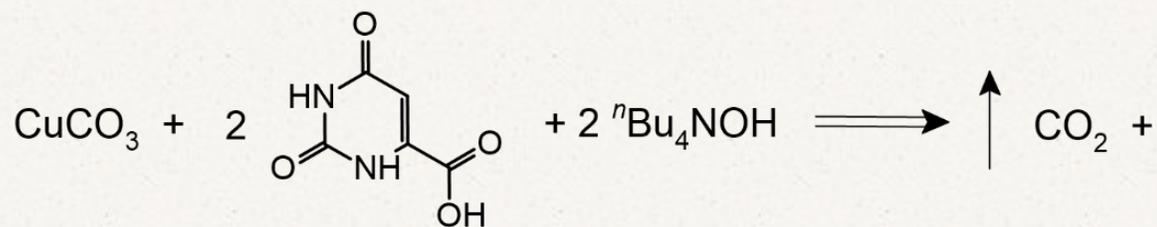
When left at room temperature in their mother liquid, the blue-green needle-like crystals of I diminish in size and eventually disappear, while large block-shaped dark blue crystals of a second form, II, appear. ② These were characterized at room temperature. Their space group is $P2_1/c$, $V = 2525.7$ (3) \AA^3 , $Z = 2$; the cell constants of **form II do not bear any obvious relationship to those of I. In form II the four-coordinate Cu complex is rigorously planar.** ③ The displacement ellipsoids are noticeably elongated perpendicular to the plane, while the displacement ellipsoids of the organic cation do not show this trend. **DFT calculations (DFT / M06 / SDD+f, 6-311++g**) ④ reveal a slight energetic advantage for the distorted conformation of the complex; so crystals of form II, which according to Ostwald's Rule are more stable than those of form I, must be energetically favored as a result of more favorable intermolecular interactions.** When selected hydrogen bonds are considered in the DFT calculations, there is almost no energy difference between the arrangements involving the two conformations.

Structure determination of I at $T = 150$ K yields the same distorted structure for the metal environment as that observed at room temperature.

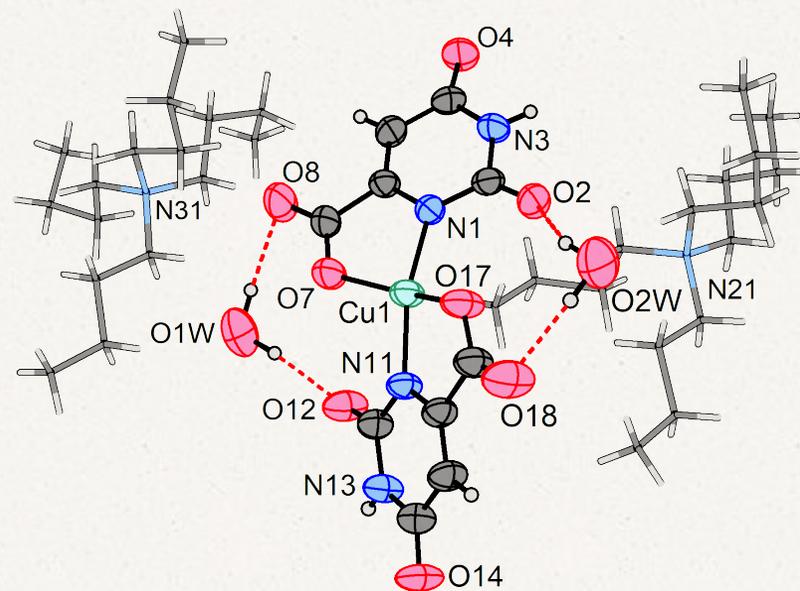
Photos from a video of the evolution of the needle-like crystals of I to the block-shaped crystals of II show the progression of the transformation. ②

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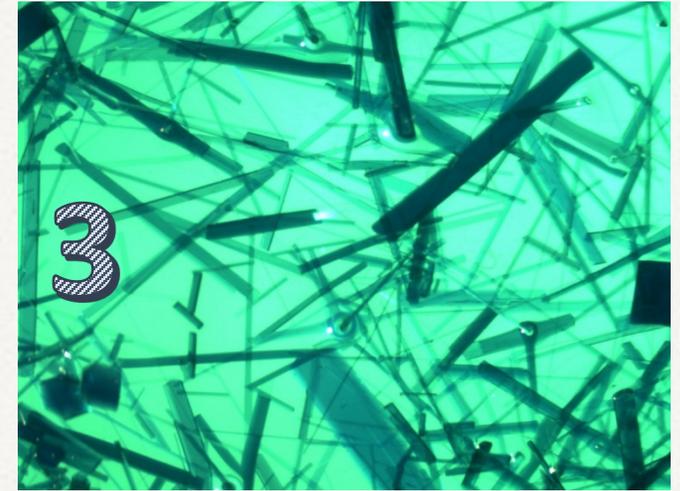
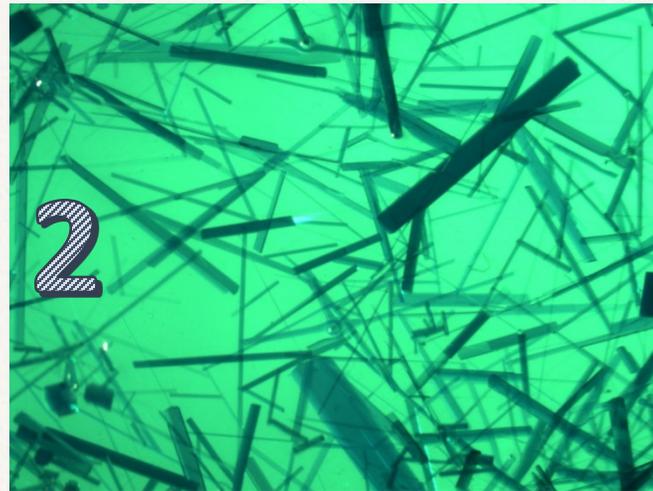
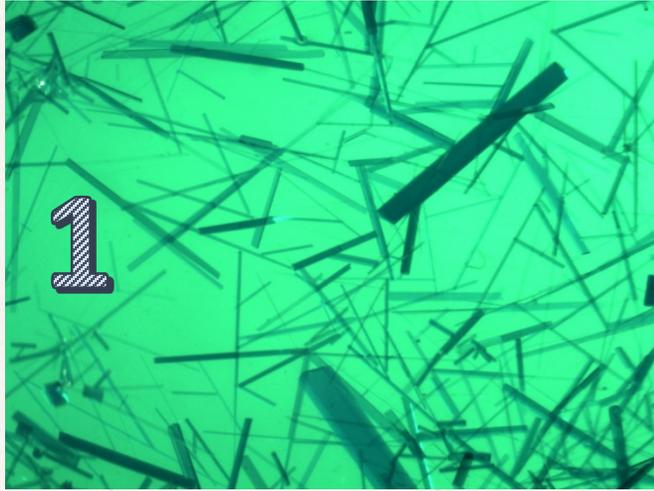
① Copper carbonate, orotic acid and tetra-*n*-butylammonium hydroxide react in water to give (*n*Bu₄N)₂[Cu(orot)₂]·2H₂O (H₂orot is orotic acid, C₅H₄N₂O₄), which crystallized in space group *P*2₁/*n*, *V* = 4913.2 (4) Å³, *Z* = 4; it was structurally characterized at room temperature. In this product, **form I, the coordination environment of the Cu center is distorted from planar geometry.** [$\tau_4 = 0.34$ Yang, L., *et al.* (2007). *Dalton Trans.* 955-964. DOI: 10.1039/b617136b]



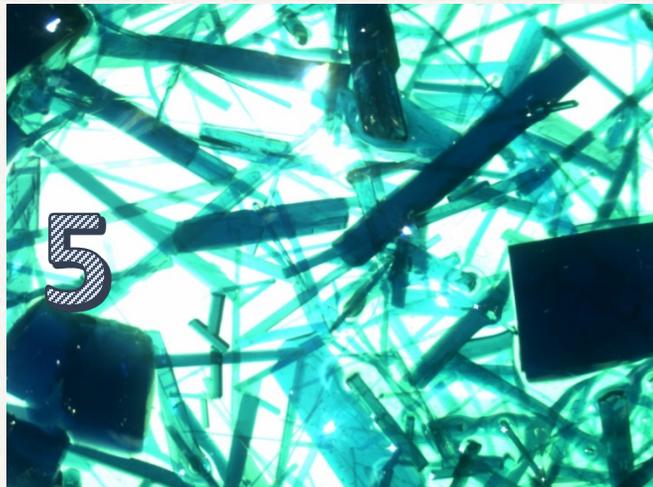
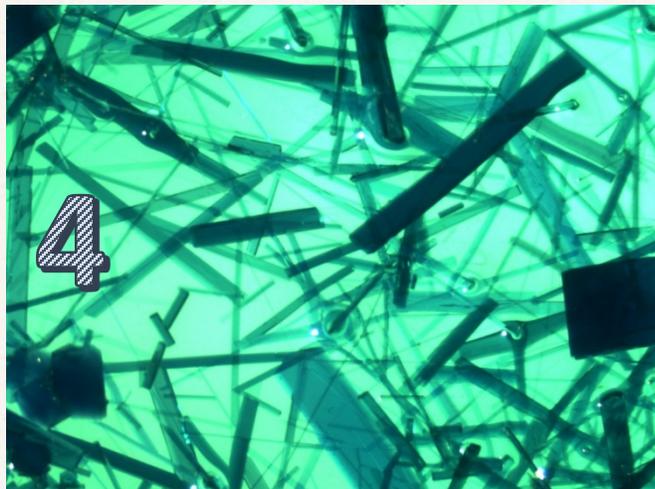
O7---Cu1---O17 152.14 (14)°



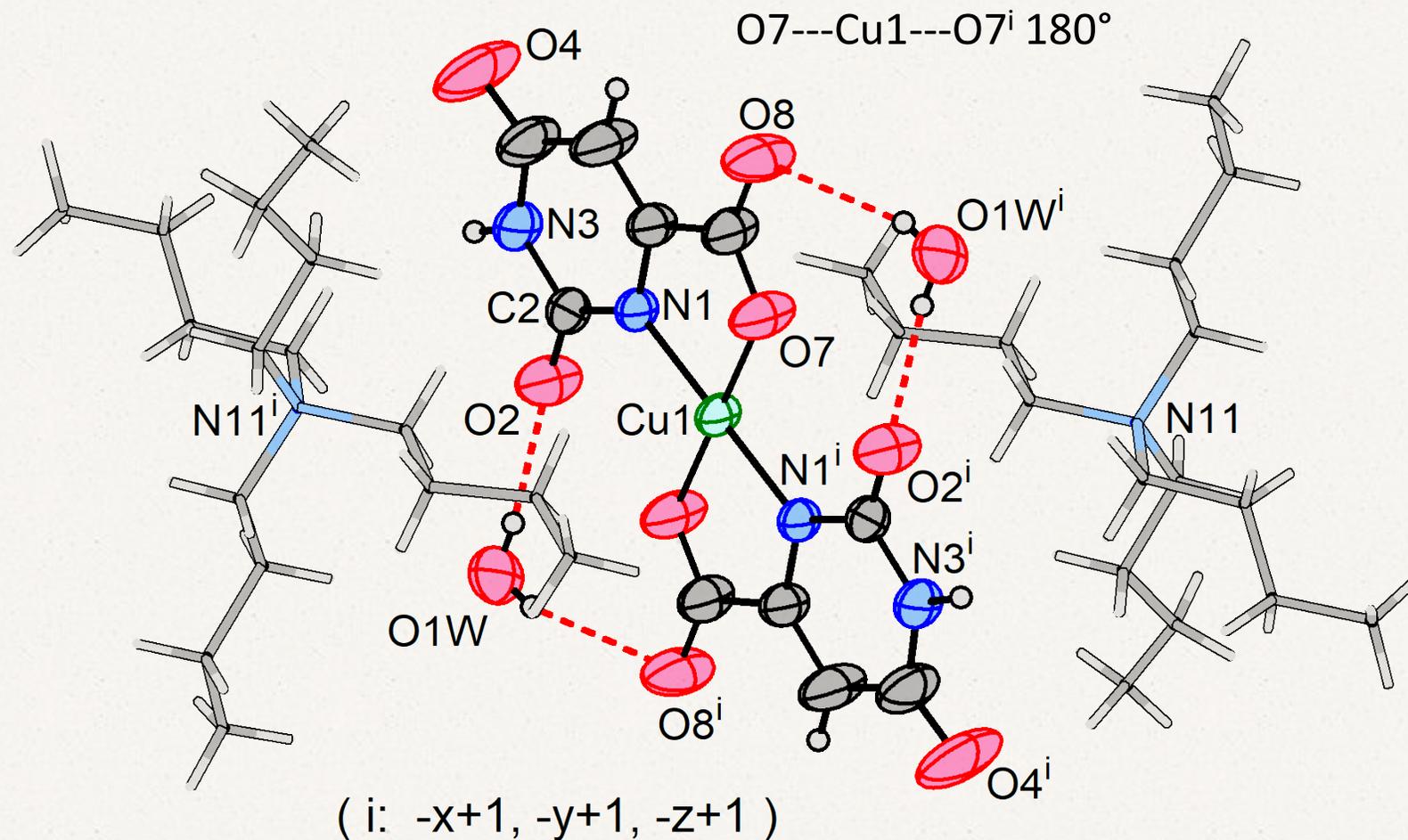
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time

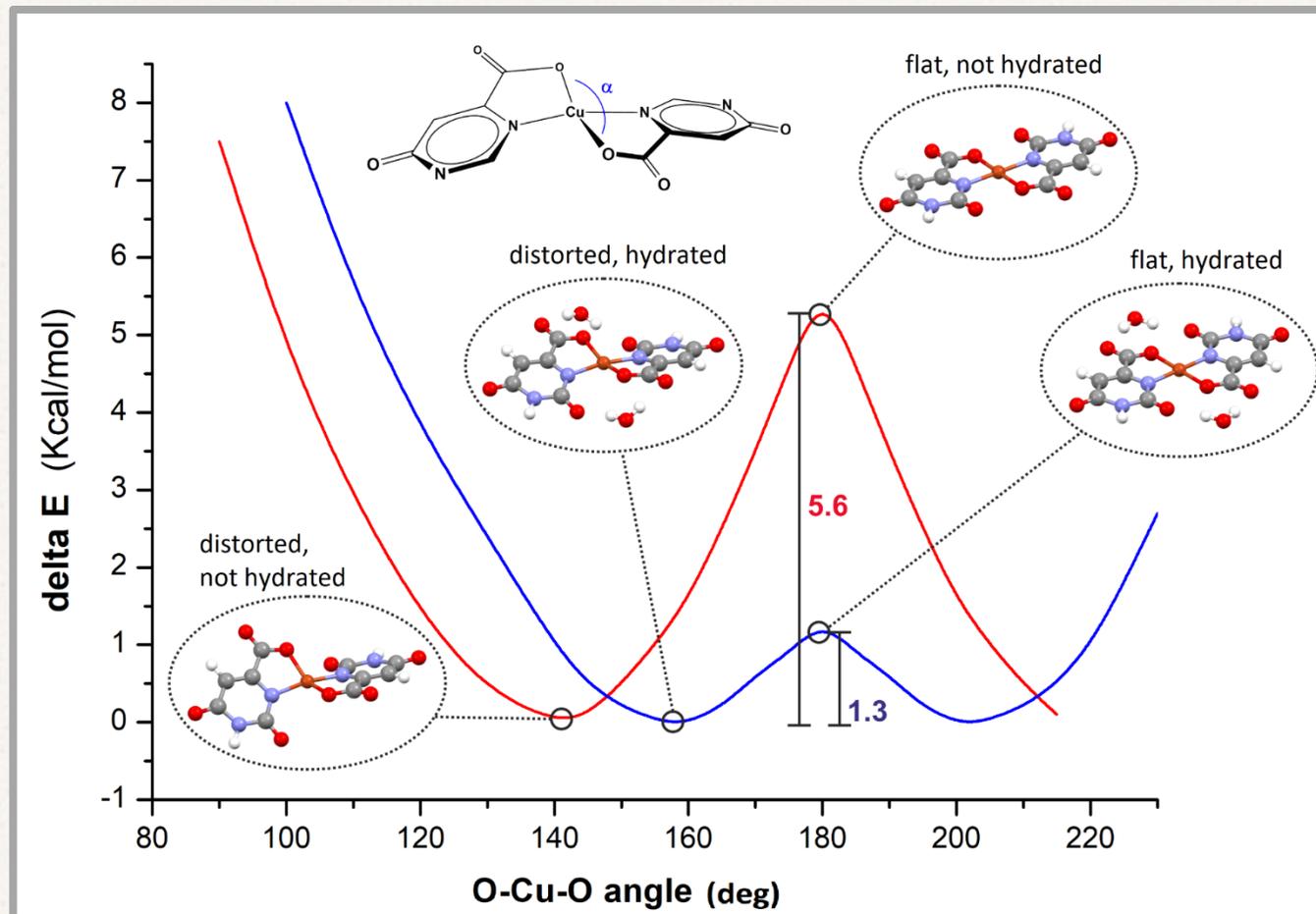


③ Crystals of form II were characterized at room temperature. Their space group is $P2_1/c$, $V = 2525.7(3) \text{ \AA}^3$, $Z = 2$; the cell constants of **form II do not bear any obvious relationship to those of I**. In form II the **four-coordinate Cu complex is rigorously planar**. The displacement ellipsoids are noticeably elongated perpendicular to the plane, while the displacement ellipsoids of the organic cation do not show this trend.



④ DFT calculations (DFT / M06 / SDD+f, 6-311++g**) reveal a slight energetic advantage for the distorted conformation of the complex; so crystals of form II, which according to Ostwald's Rule are more stable than those of form I, must be energetically favored as a result of more favorable intermolecular interactions. When selected hydrogen bonds are considered in the DFT calculations, there is almost no energy difference between the arrangements involving the two conformations.

DFT / M06 / SDD+f, 6-311++g**
Incorporating the nearest H-bonding partners into the calculation has a greater stabilizing effect on the flat conformation, relative to that on the nominally more stable distorted form.



Further Information

Structure determination of **I** at T = 150 K yields the same distorted structure for the metal environment as that observed at room temperature.

form	1	1	2
T, K	150 (2)	298 (2)	298 (2)
a, Å	23.1579(8)	23.2179(10)	10.0835(5)
b, Å	8.1202(2)	8.3932(4)	14.7363(10)
c, Å	25.4979(9)	25.5570(12)	17.0729(9)
β , deg	98.923(3)	99.420(4)	95.390(5)
v, Å ³	4736.7(3)	4913.2(4)	2525.7(3)
space group	P2 ₁ /n	P2 ₁ /n	P2 ₁ /c
O---Cu---O, deg	153.73(11)	152.14 (14)	180
tau(4)	0.35	0.34	0.00
tetrahedral volume, Å ³	1.950	1.918	0.00
quadratic elongation	1.553	1.562	---
angle variance, deg ²	1142.18	1158.54	---

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