

Supporting Information

for

Differential Reactivity Between Two Copper Sites in Peptidylglycine α -Hydroxylating Monooxygenase (PHM)

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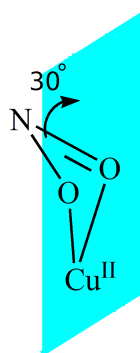


Figure S1. Angular orientation of the $\text{Cu}_M\text{-O}_2\text{N}$ moiety of the nitrite-soaked PHMcc crystal.

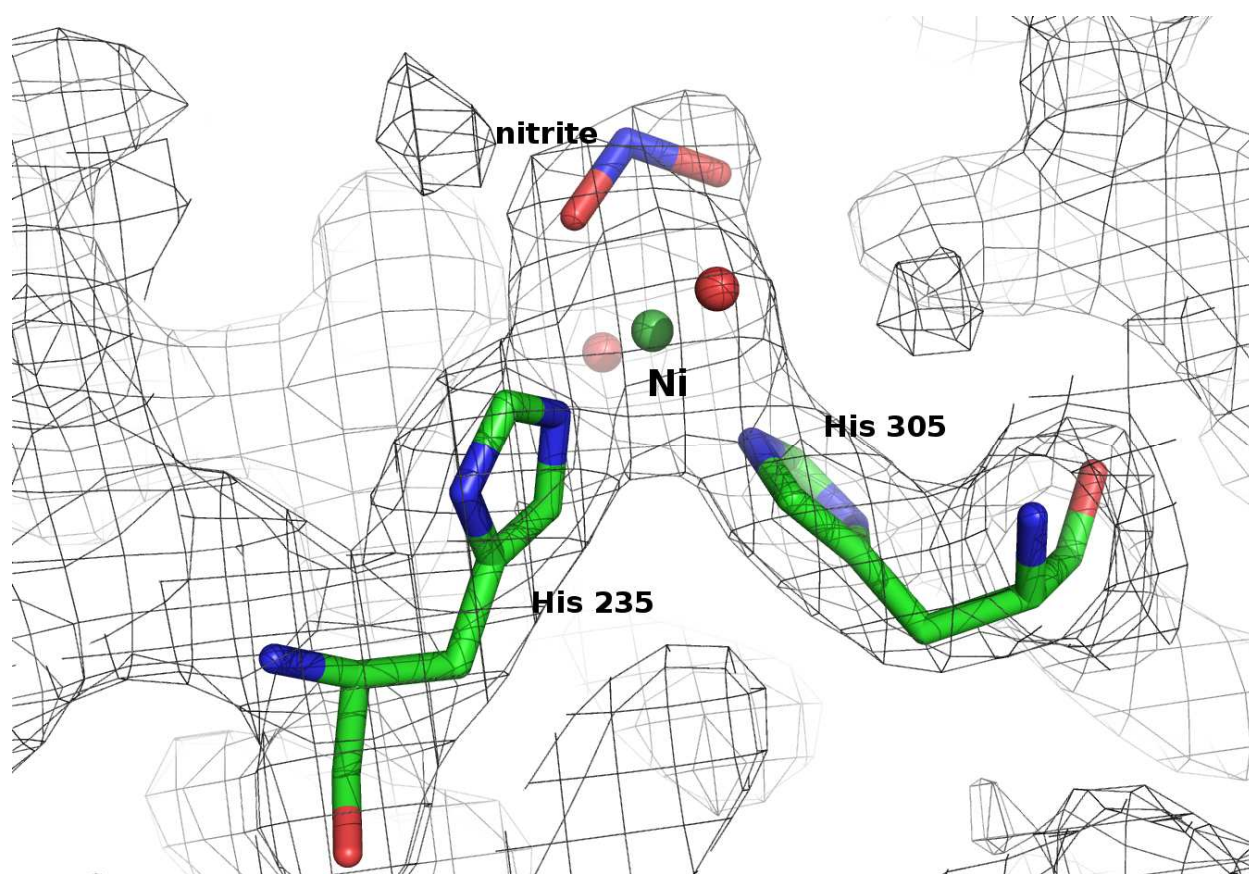


Figure S2. The structure of the Ni crystal contact of a nitrite-soaked PHMcc. Ni^{II} ion is found in an octahedral environment with nitrite bound to the metal in an asymmetric bidentate fashion (Ni-O_{nitrite} = 1.95 and 2.65 Å). A grey mesh represents 2Fo-Fc electron density contoured at 1.0 σ . Carbons (green), nitrogens (blue), oxygens (red), nickel (green ball) and water molecules (red balls) are colored as indicated.

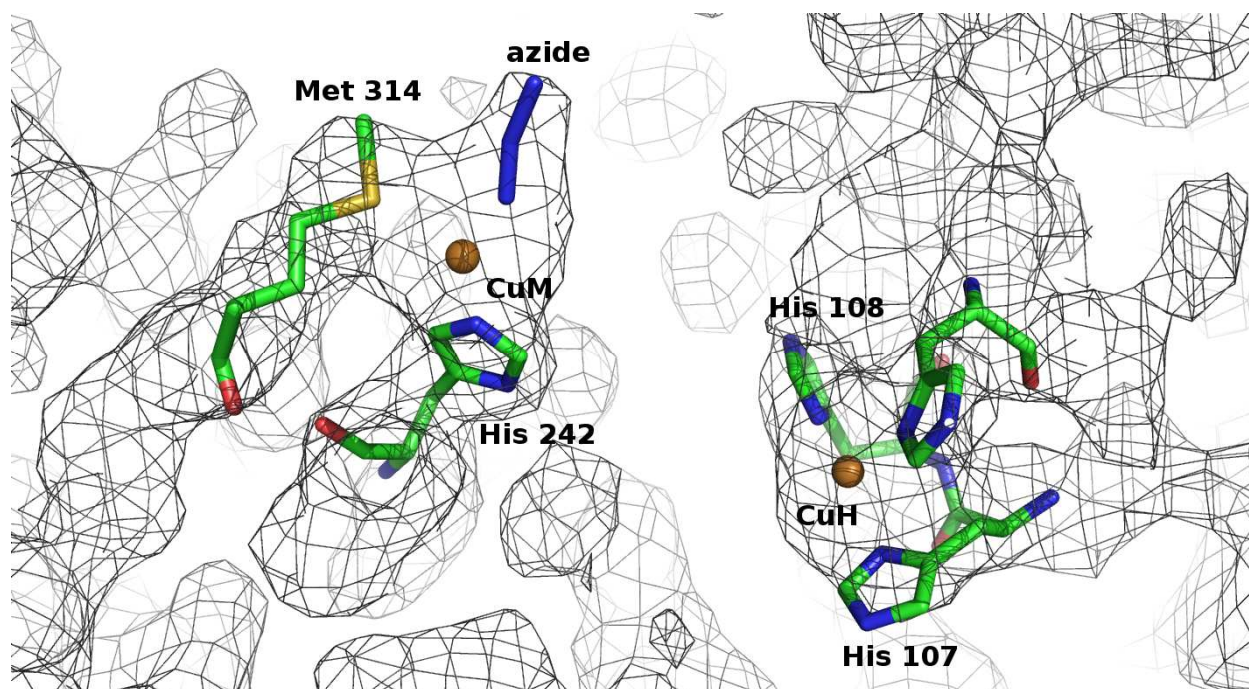


Figure S3. The structure of Cu_M and Cu_H sites of an azide-soaked PHMcc. Soaking conditions: 100 mM NaN_3 for 1.5 hours. The azide is shown bound to Cu_M at 1.8 Å. The Cu_M ligand His 244 is not shown in the figure for clarity. A gray mesh represents 2Fo-Fc electron density contoured at 1.0 σ . Carbons are colored green, nitrogens blue, oxygens red, sulphur yellow and copper gold.

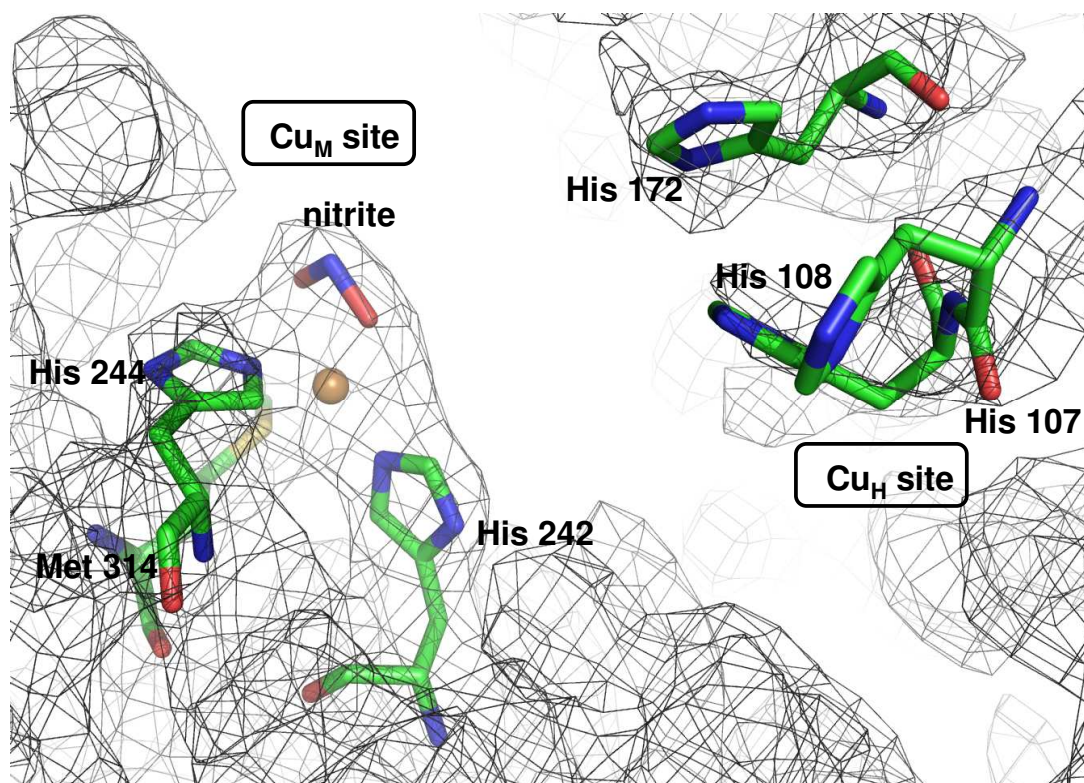


Figure S4. The structure of the Cu_M site of a reduced nitrite-soaked PHMcc. The nitrite is shown bound to Cu_M while the Cu_H has been completely removed by effect of the high concentration of nitrite. A gray mesh represents $2F_o - F_c$ electron density contoured at 1.0σ . Carbons are colored grey, nitrogens blue, oxygens red, sulphur yellow and copper green.

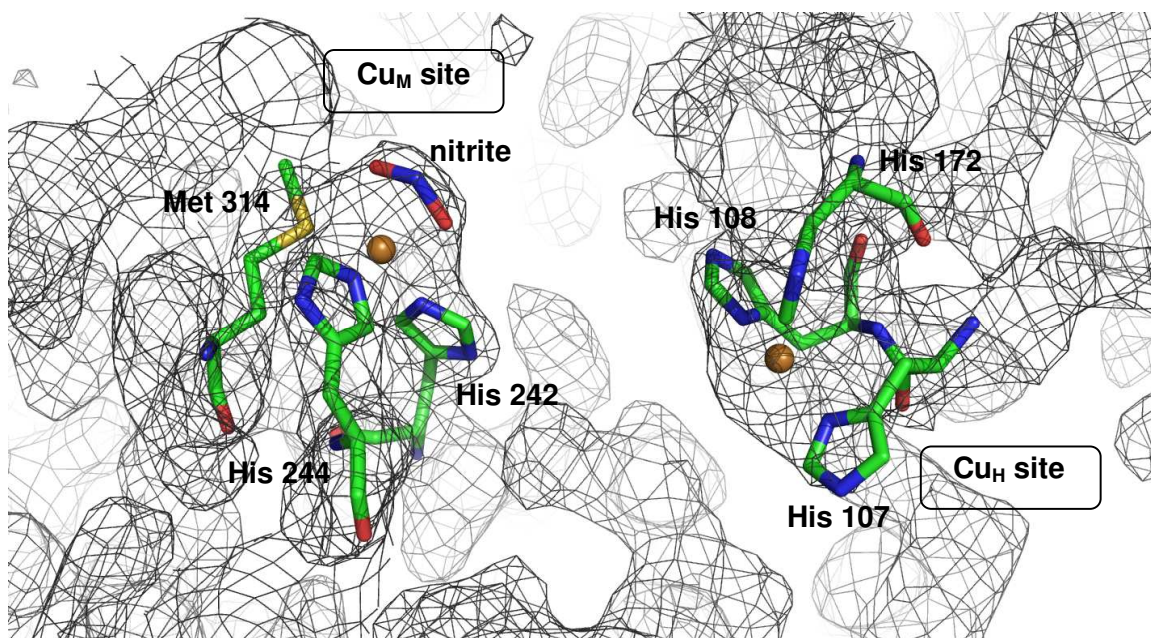


Figure S5. The structure of Cu_M and Cu_H sites of a nitrite-soaked PHMcc in the presence of substrate. The nitrite is shown bound to Cu_M as a bidentate ligand. A gray mesh represents $2F_o - F_c$ electron density contoured at 1.0σ . Carbons are colored green, nitrogens blue, oxygens red, sulfur yellow and copper gold.