

**Pyrazolate-based copper(II) and nickel(II) [2 × 2] grid complexes:
protonation-dependent self-assembly, structures and properties**

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Supplementary material

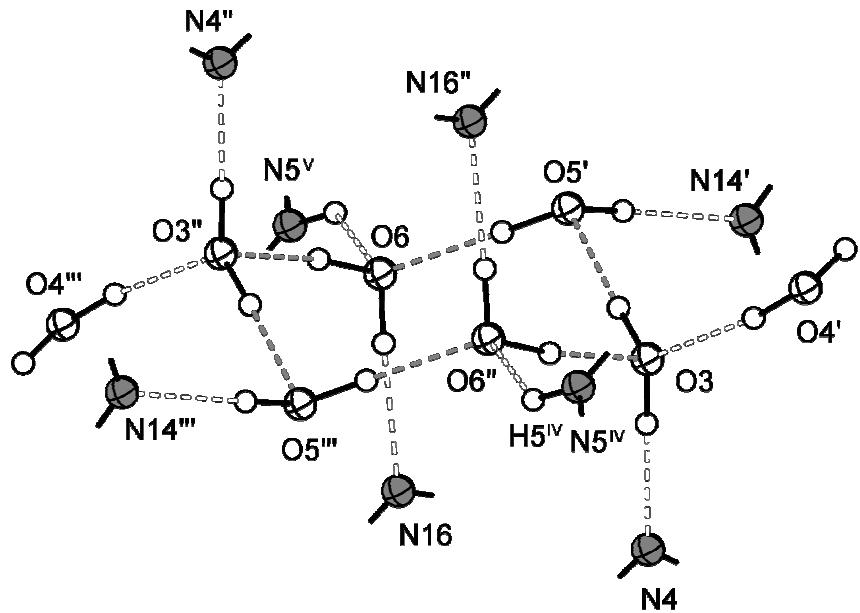


Figure S1. Plot of a part of the hydrogen-bonding network of H_3L . Selected interatomic distances (\AA) and angles ($^\circ$): $\text{O}3\cdots\text{O}5'$ 2.700(2), $\text{O}5'\cdots\text{O}6$ 2.765(2), $\text{O}6\cdots\text{O}3''$ 2.764(2); $\text{O}3-\text{H}3\text{B}\cdots\text{O}5'$ 175(3), $\text{O}5'-\text{H}5\text{B}'\cdots\text{O}6$ 175(2), $\text{O}6-\text{H}6\text{B}\cdots\text{O}3''$ 173(2), $\text{O}6''\cdots\text{O}3\cdots\text{O}5'$ 93.28(5), $\text{O}5'\cdots\text{O}6\cdots\text{O}3''$ 110.24(6), $\text{O}6\cdots\text{O}3''\cdots\text{O}5'''$ 109.90(5). Symmetry transformations used to generate equivalent atoms (''): $1+x, -1+y, 1+z$; ('''): $2-x, -y, 2-z$; (''''): $1-x, 1-y, 1-z$; (^{IV}): $2-x, 1-y, 1-z$; (^V): $x, -1+y, 1+z$.

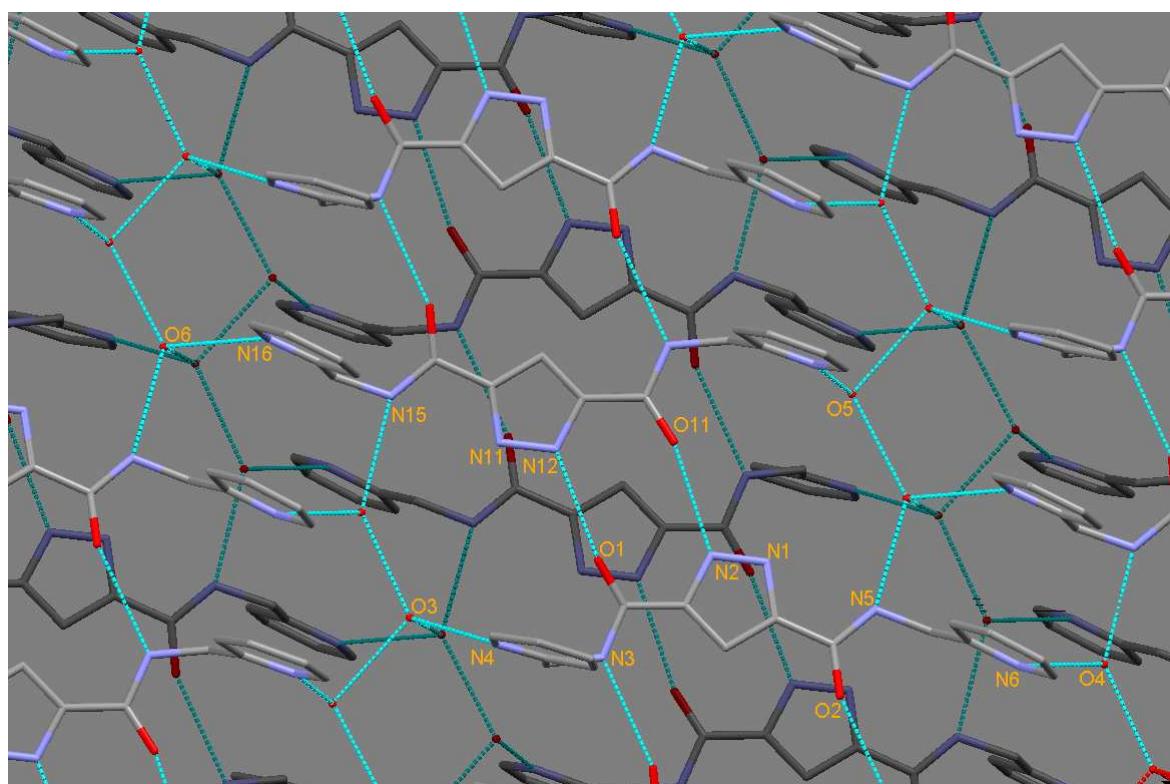


Figure S2. Plot of the hydrogen-bonding network of H_3L .

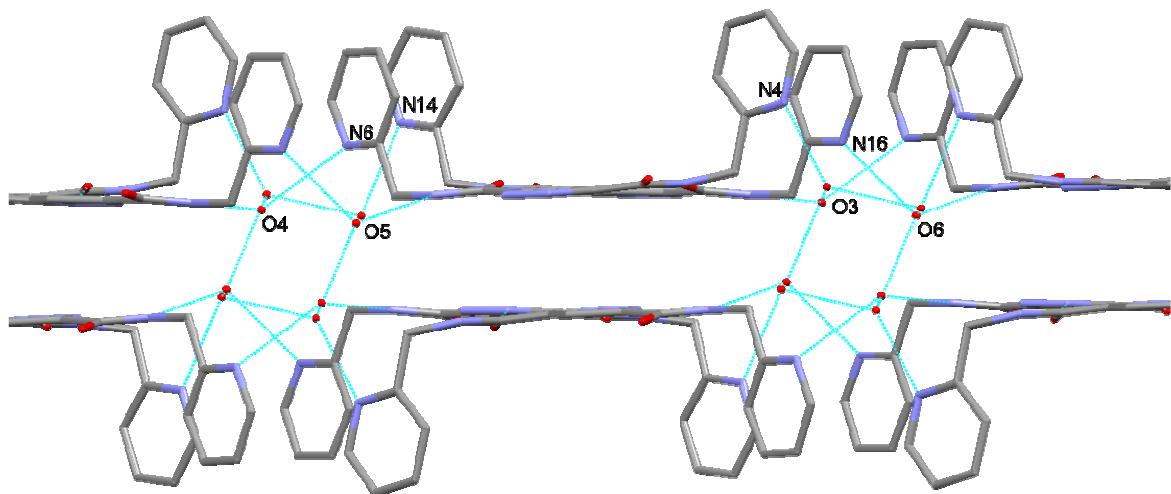


Figure S3. Plot of the hydrogen-bonding network of H_3L .

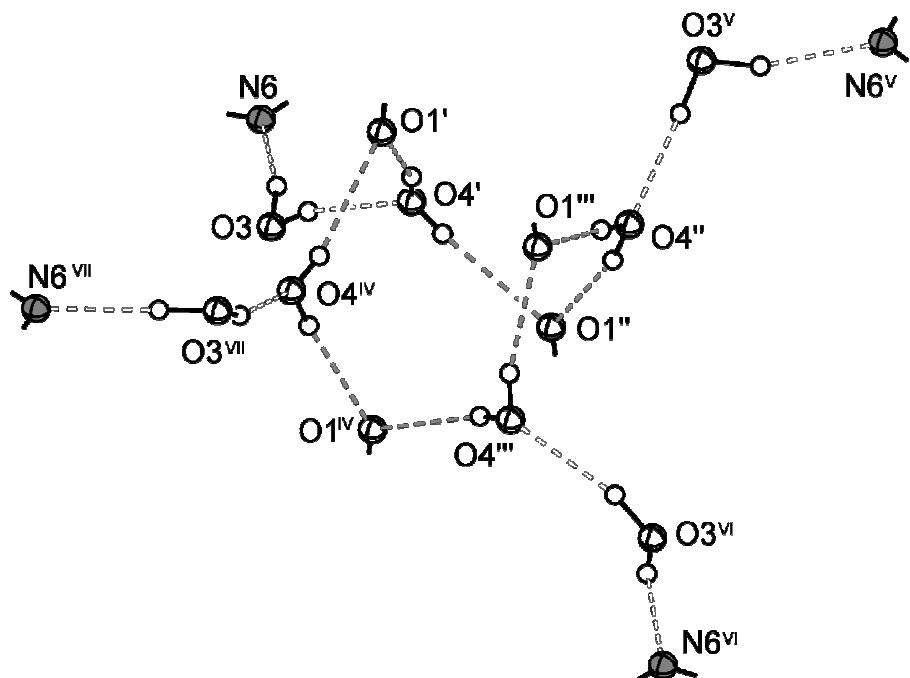


Figure S4. Plot of a part of the hydrogen-bonding network of $[\text{Cu}_4(\text{HL})_4]$. Selected interatomic distances (\AA) and angles ($^\circ$): $\text{O}3\cdots\text{N}6$ 2.777(4), $\text{O}3\cdots\text{O}4'$ 2.819(4), $\text{O}4'\cdots\text{O}1'$ 2.758(3), $\text{O}4'\cdots\text{O}1''$ 2.879(3); $\text{O}3\cdots\text{H}3\text{A}\cdots\text{N}6$ 163(3), $\text{O}3\cdots\text{H}3\text{B}\cdots\text{O}4'$ 163(4), $\text{O}4'\cdots\text{H}4\text{A}'\cdots\text{O}1'$ 164(4), $\text{O}4'\cdots\text{H}4\text{B}'\cdots\text{O}1''$ 168(4), $\text{O}1'\cdots\text{O}4'\cdots\text{O}1''$ 108.9(1), $\text{O}4'\cdots\text{O}1''\cdots\text{O}4''$ 88.8(1). Symmetry transformations used to generate equivalent atoms (''): $-0.5+x, y, 0.5-z$; (''): $0.75-y, 0.25+x, 0.25+z$; ('') $0.5-x, 1.5-y, 0.5-z$; ('^{IV}') $0.75+y, 1.25-x, 0.25+z$; ('^V') $0.75-y, 0.75+x, 0.75-z$; ('^{VI}') $-x, 1.5-y, z$; ('^{VII}') $0.75+y, 0.75-x, 0.75-z$.

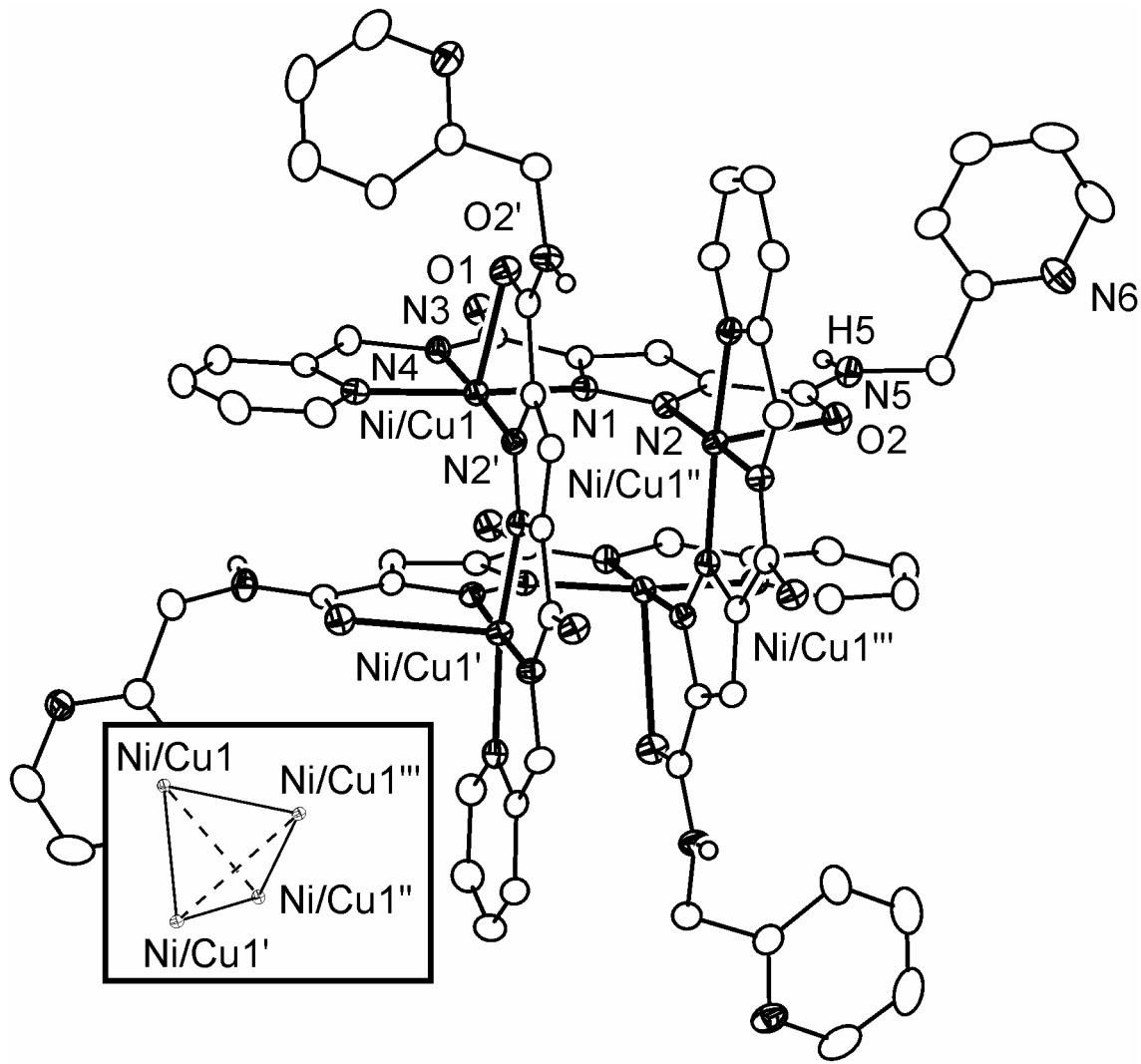


Figure S5. Plot of the molecular structure of $[\text{Cu}_2\text{Ni}_2(\text{HL})_4]$. For the sake of clarity all hydrogen atoms except the N–H protons and the water molecules have been omitted. The inset shows the tetrahedral nickel/copper core. Selected interatomic distances (\AA) and angles ($^\circ$): Ni/Cu1–N1 1.940(2), Ni/Cu1–N3 1.895(2), Ni/Cu1–N4 1.965(2), Ni/Cu1–N2' 1.936(2), Ni/Cu1–O2' 2.543(2), Ni/Cu1…Ni/Cu1''//Ni/Cu1…Ni/Cu1'''//Ni/Cu1'…Ni/Cu1''//Ni/Cu1''…Ni/Cu1''' 4.0054(5), Ni/Cu1…Ni/Cu1''//Ni/Cu1'…Ni/Cu1''' 4.5643(6); N1–Ni/Cu1–N3 82.05(8), N1–Ni/Cu1–N4 164.13(7), N1–Ni/Cu1–N2' 97.11(8), N1–Ni/Cu1–O2' 95.76(7), N3–Ni/Cu1–N4 82.39(8), N3–Ni/Cu1–N2' 177.75(8), N3–Ni/Cu1–O2' 108.68(7), N4–Ni/Cu1–N2' 97.11(8), N4–Ni/Cu1–O2' 92.14(7), N2'–Ni/Cu1–O2' 73.51(7). Symmetry transformations used to generate equivalent atoms ('): 1.25– y , 0.25+ x , 1.25– z ; (''): 1– x , 1.5– y , z ; ('''') –0.25+ y , 1.25– x , 1.25– z .