Electronic Supplementary Information for Dalton Transactions

Structure and Dimensionality of Coordination Complexes Correlated to Piperazine Conformation: From Discrete $[Cu^{II}_2]$ and $[Cu^{II}_4]$ Complexes to a $\mu_{1,3}$–N_3^- Bridged $[Cu^{II}_2]_n$ Chain

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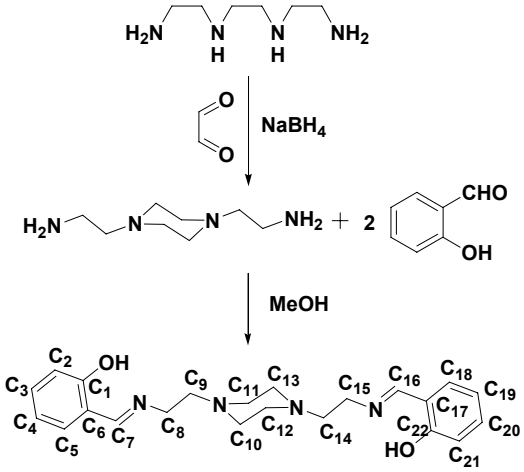
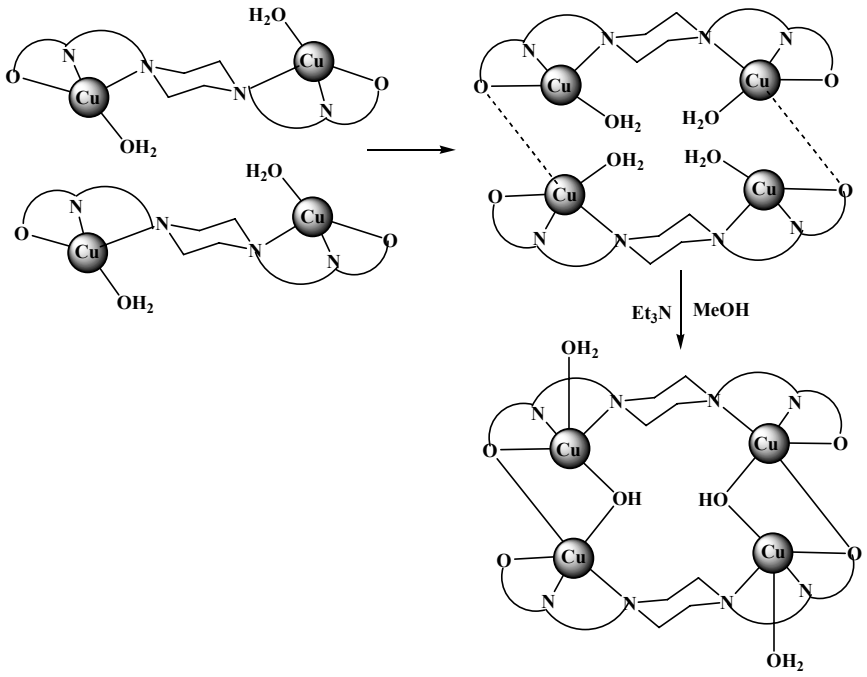


Scheme S1



Scheme S2

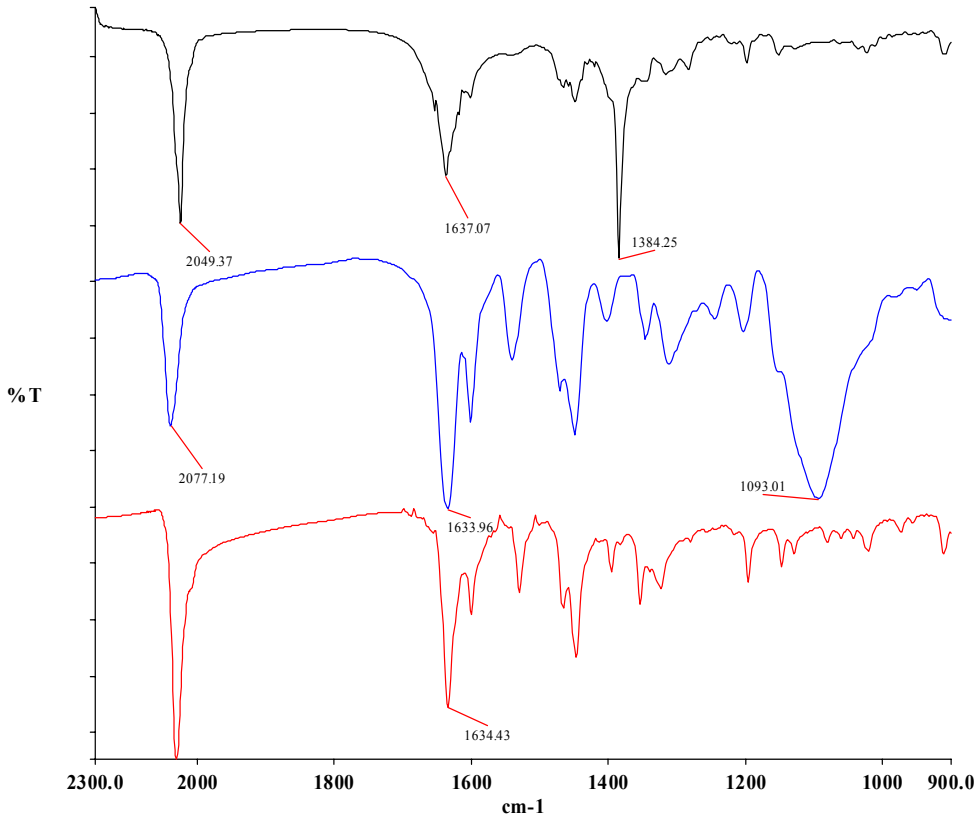


Figure S1. FT-IR spectra of complexes **3b** (top), **3a**(middle) and **4** (bottom).

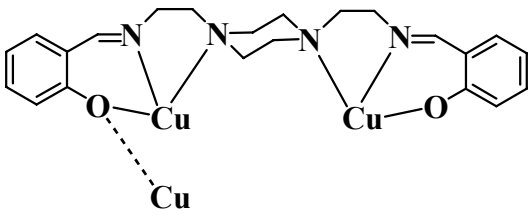


Figure S2. Schematic representation of the asymmetric bridging mode (μ_3) of ligand L^{2-} in complexes **2a** and **2b**.

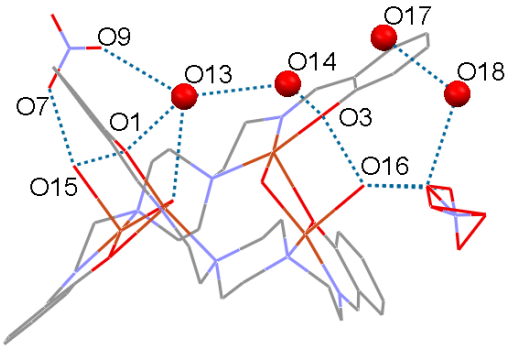


Figure S3. Intra- and intermolecular hydrogen bonding network exhibited by complex **2b**.

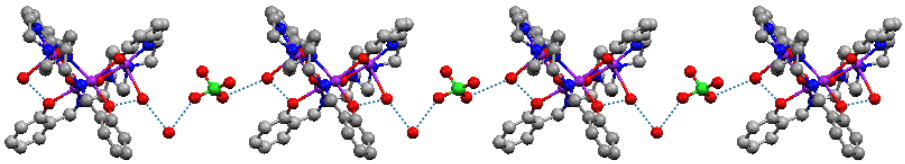


Figure S4. Hydrogen bonding network in **2a** viewed along the crystallographic a-axis.

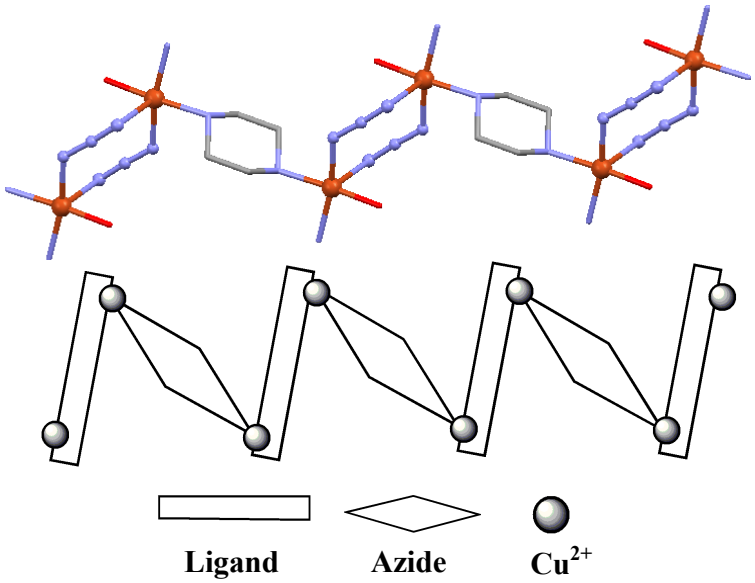


Figure S5. The metal to metal connectivity in **4,** achieved through azido and piperazine bridging fragments.

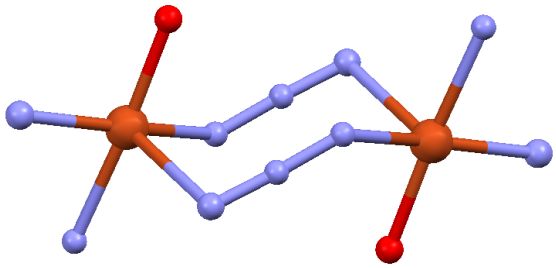


Figure S6. Representation of the [Cu(μ-N_3)$_2$Cu] core of complex **4**, emphasizing its *chair* conformation, where six azide nitrogen atoms lie in one plane.

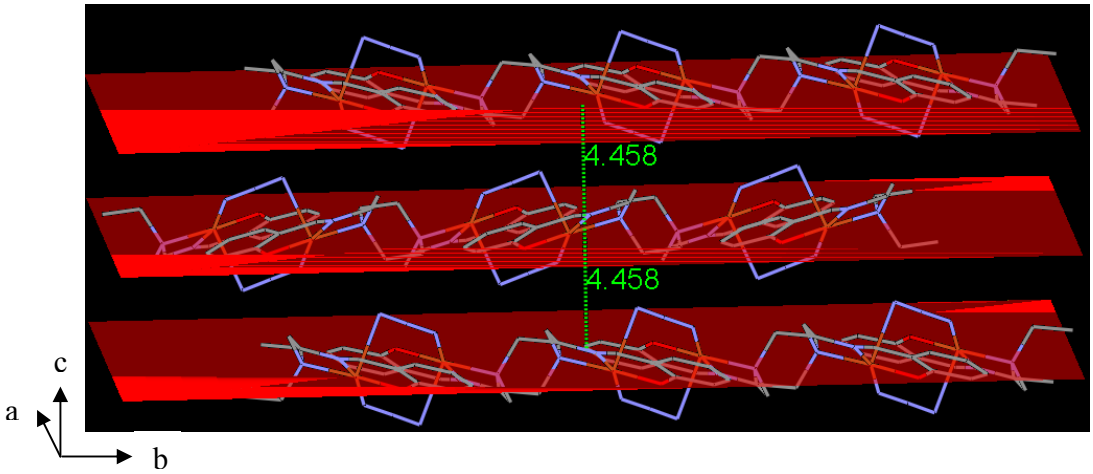


Figure S7. Representation of the 1D chain propagation in **4** along the crystallographic *b*-axis with an inter-planar distance of 4.458 Å.

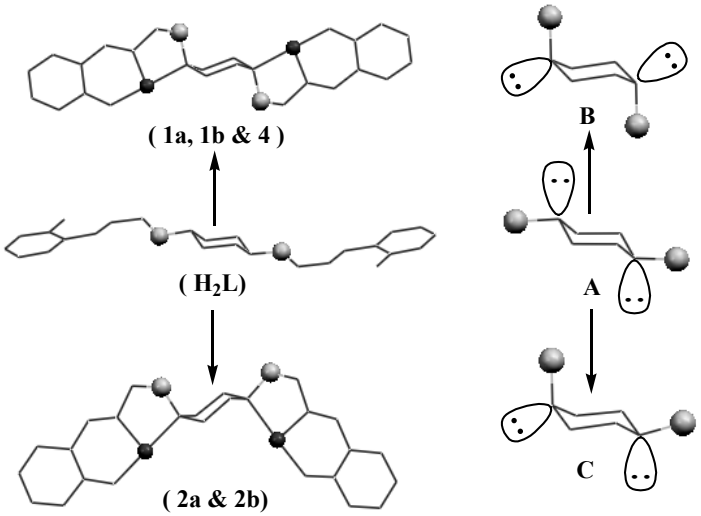


Figure S8. Left; molecular solid state structure of H_2L (middle), together with that of the $[Cu_2L]$ unit of **1a/b** and **4** (top) and the analogous fragment of **2a/b** (bottom). Right; schemes of the conformation of the piperazine fragment in each compound, where the orientation of N-atom lone pairs are indicated. Grey balls = α–C atoms, black ball = Cu.