

Computational Details

Full geometry optimizations were performed on $[\text{Cu}_2(\text{hpp})_2\text{Cl}_2]$, **1**. All calculations were performed with the Gaussian 03 (G03) suite of programs¹ using a triple- ζ quality Pople basis set with a diffuse and polarization function on the heavy atoms (6-311+G(d))² for Cl, C, N, and H and a triple- ζ quality basis set (SDD) with a small core effective core potential (ECP)³ for the Cu atoms (BSI). Geometry optimizations were performed using Density-Functional Theory (DFT)⁴ with the B3LYP (Becke three-parameter hybrid exchange functional⁵ and the Lee-Yang-Parr correlation functional)⁶ and MPW1PW91 (Barone's Modified Perdew-Wang 1991 exchange functional and Perdew and Wang's 1991 correlation functional)⁷ and second-order Møller-Plesset perturbation theory (MP2).⁸ The Raman calculation was performed at the MPW1PW91 level of theory using BSI with the addition of a diffuse and polarization function for the hydrogen atoms (6-311++G(d,p)).² The MPW1PW91/BSI optimized structure of **1**, was used for the Raman calculation.

Computational Discussion

The MPW1PW91/BSI optimized structure of **1** (Figure S11), calculates a Cu-Cu bond distance (2.87 Å) that is 0.2 Å longer than the crystal structure (2.67 Å), which is consistent with the underestimation of dispersion forces by DFT.⁹ To validate the MPW1PW91/BSI model, **1** was also optimized at the MP2/BSI level (Figure S11). Interestingly, the MP2/BSI Cu-Cu bond distance (3.01 Å) was calculated to be 0.34 Å longer than the crystal structure (2.67 Å). Both the MPW1PW91/BSI and MP2/BSI optimized structures have shorter Cl-N bond distances than the crystal structure of **1**

(3.21Å, 3.22Å, and 3.36Å, respectively). B3LYP/BSI was also used to optimize the structure of **1** (Figure SI2) and at this level of theory, the Cu-Cu bond is completely lost (Cu-Cu bond distance of 4.74Å). An overlay of the crystal, MPW1PW91/BSI, and MP2/BSI structures of **1**, illustrates that the hpp ligands in the theoretical models move significantly from the crystal structure indicating that there may be some packing effects.

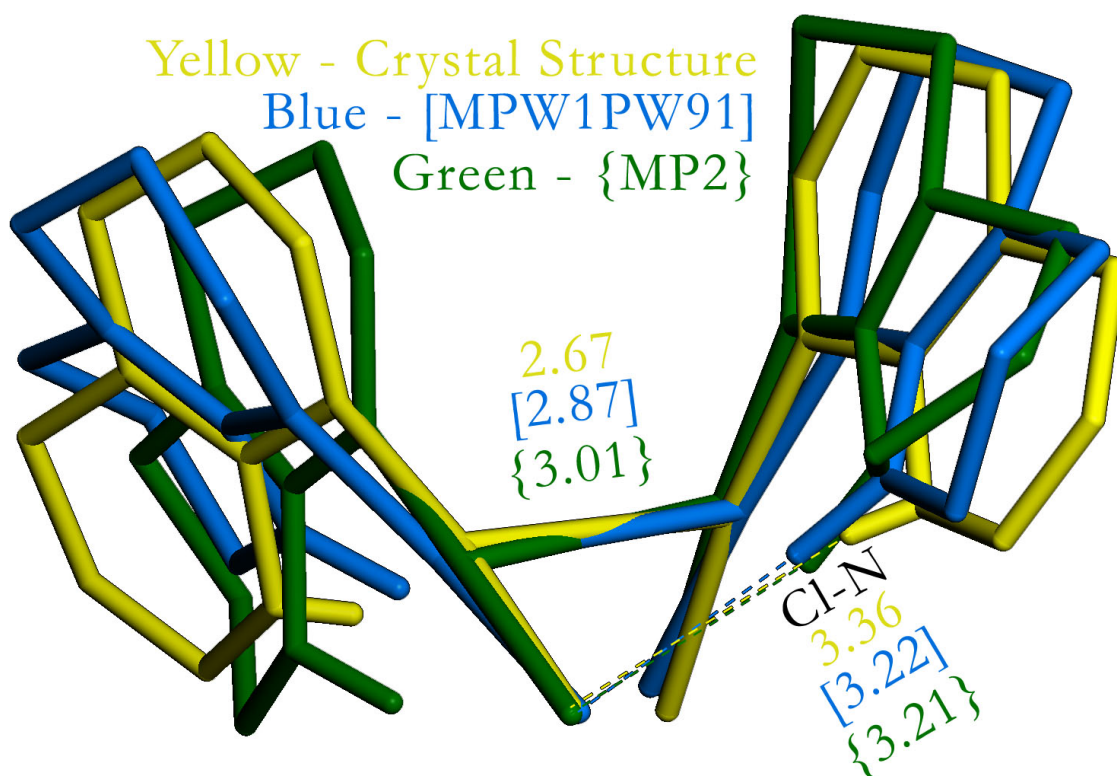


Figure SI1. Overlay of the crystal structure of **1** (yellow), MPW1PW91/BSI optimized structure (blue), and the MP2/BSI optimized structure (green). All distances are reported in Åströms.

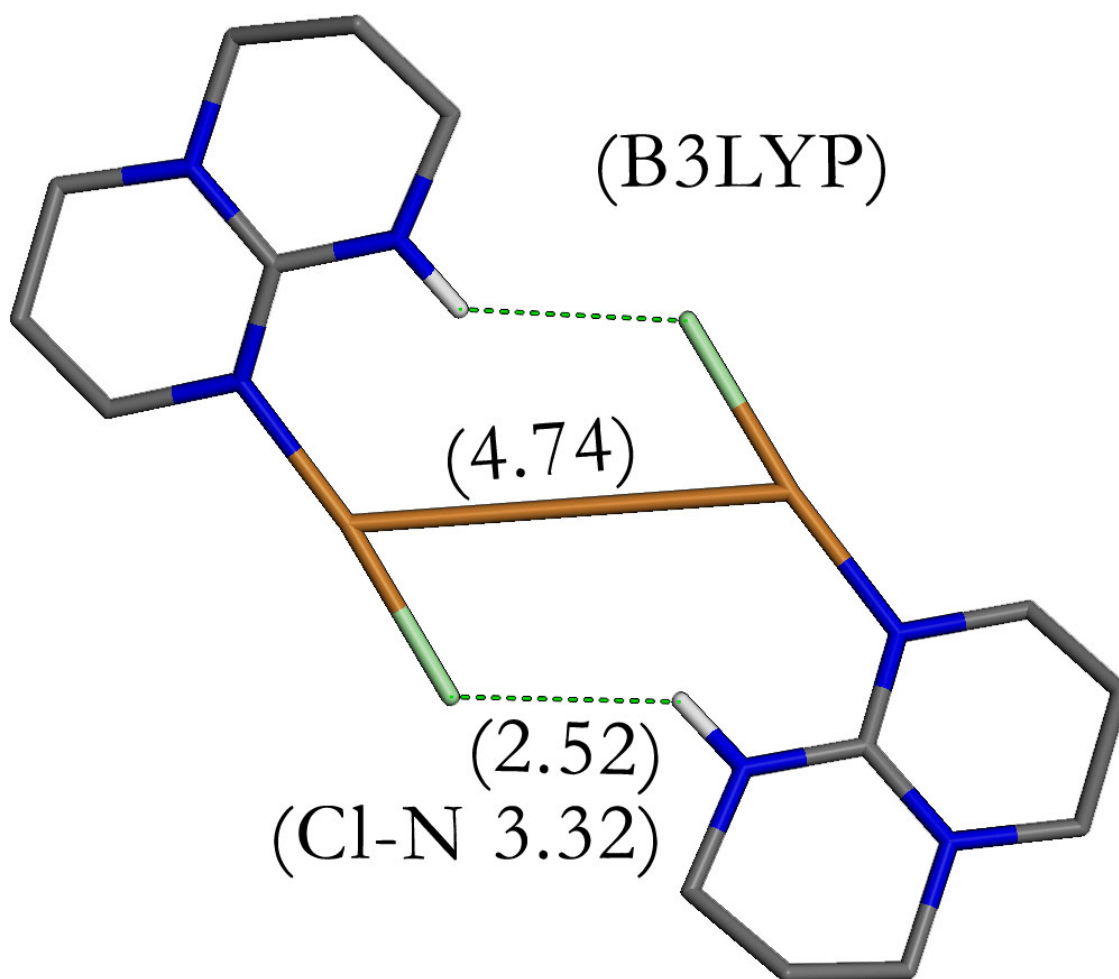


Figure SI2. B3LYP/BSI optimized structure illustrating the loss of the Cu-Cu bond. All distances are reported in Åströms.

1) Gaussian 03, Revision C.02, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A.; Gaussian, Inc., Wallingford CT, 2004.

2) (a) R. Krishnan, J.S. Binkley, R. Seeger and J.A. Pople, *J. Chem. Phys.* **72**, 650 (1980)
(b) McLean, A.D.; Chandler G.S. *J. Chem. Phys.* **1980**, *72*, 5639 (c) Frisch, M.J. ; Pople, J.A.; Binkley, J.S. *J. Chem. Phys.* **1984**, *80*, 3265.

3) Schwerdtfeger, P.; Dolg, M.; Schwarz, W.H.E.; Bowmaker, G.A.; Boyd, P.D.W. *J. Chem. Phys.* **1989**, *91*, 1762.

4) Parr, R.G.; Yang, W. *Density-Functional Theory of Atoms and Molecules*, Oxford University Press, Oxford, 1989.

5) Becke, A.J. *Chem. Phys.* **1993**, *98*, 5648.

6) Lee, C.; Yang W.; Parr, R.G. *Phys. Rev.* **1988**, *37*, 785.

7) Adamo, C.; Barone, V. *J. Chem. Phys.* **108**, 664 (1998).

8) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.

9) Pyykko, P. *Chem. Rev.* **1997**, *97*, 597.