Crystal Structure, Hirshfeld Analysis, and DFT Calculations of Three Trinuclear Cu(II) Polymorphs

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Breakdown of 2D Fingerprint Plots

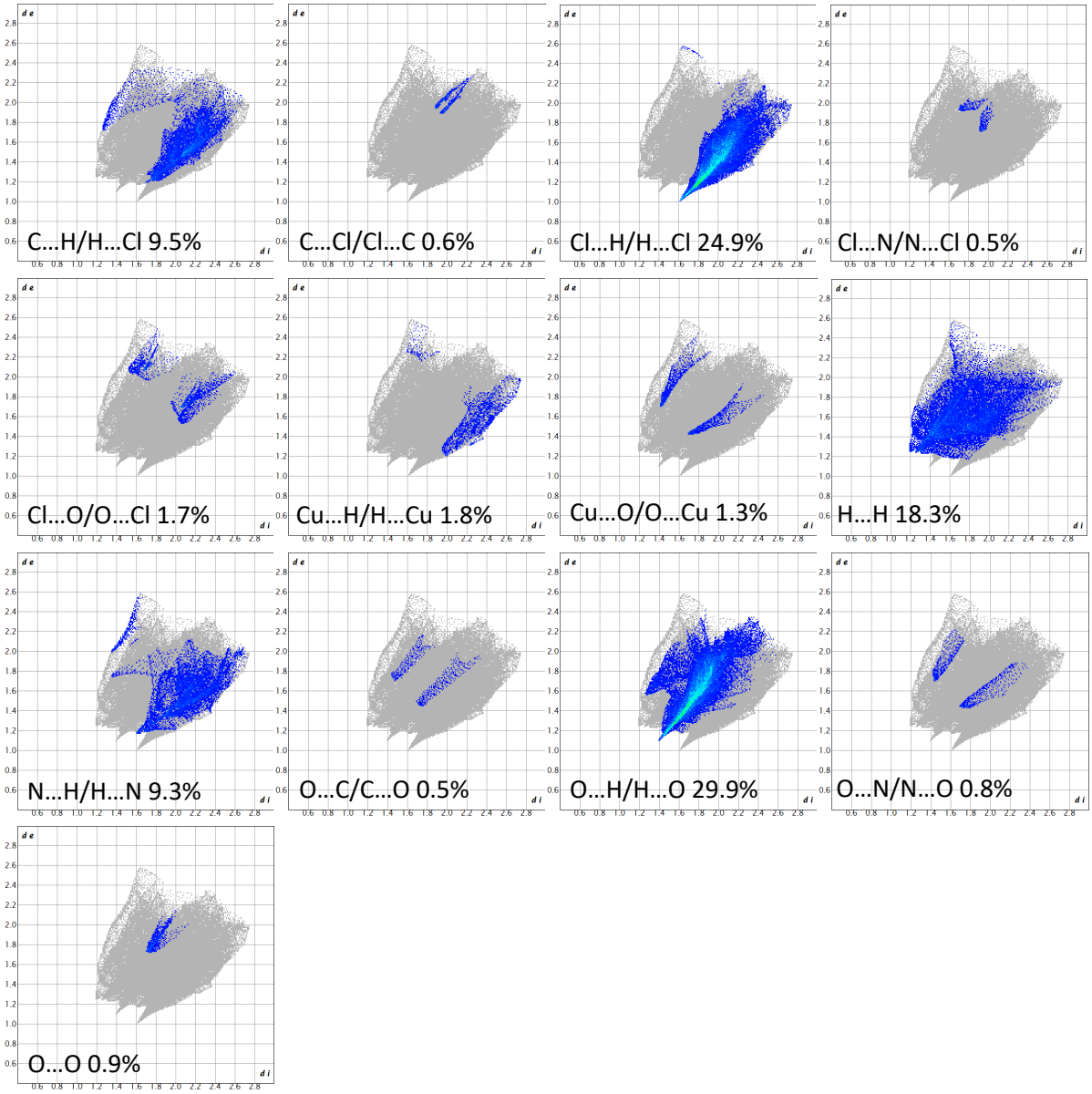


Figure S1. Breakdown of 2D fingerprint plot by type of individual atomistic contribution for complex **1a**

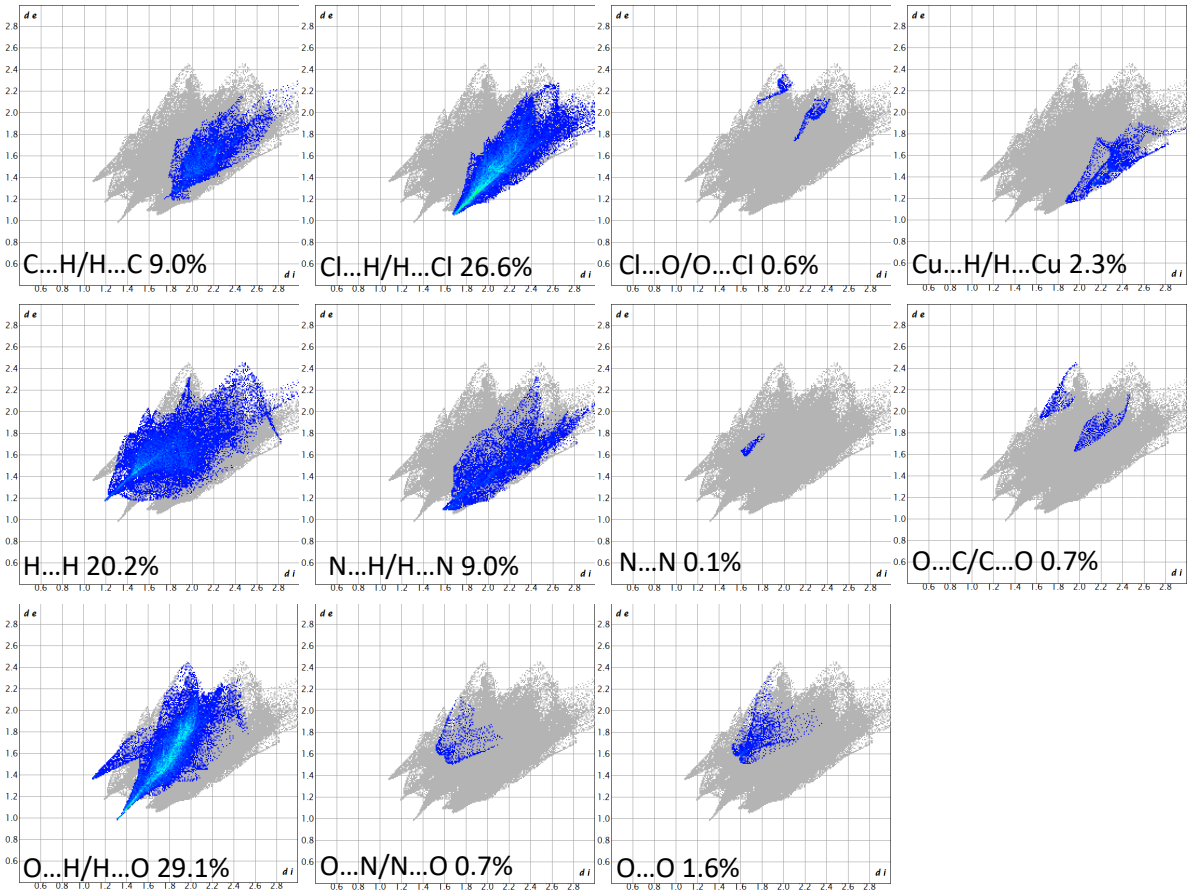
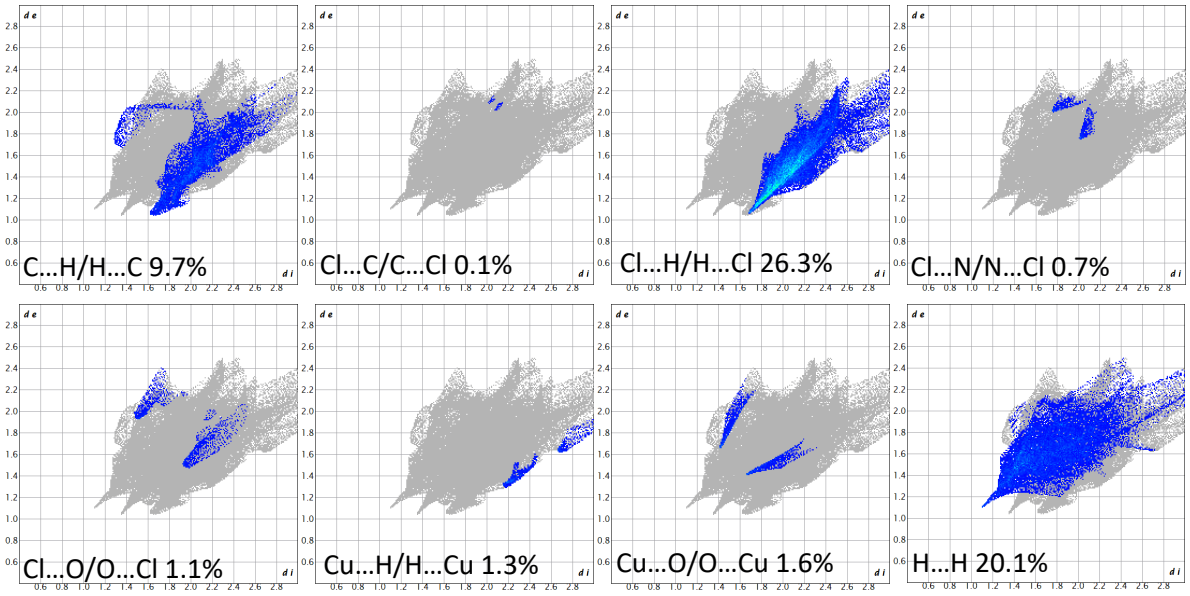


Figure S2. Breakdown of 2D fingerprint plot by type of individual atomistic contribution for complex **1b.**



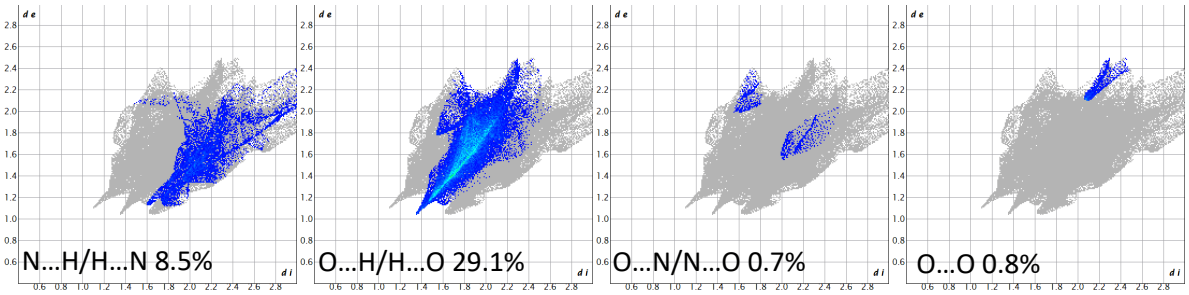


Figure S3. Breakdown of 2D fingerprint plot by type of individual atomistic contribution for complex **1c.**

Hirshfeld Surface Analysis (Figures 5, 6, and 7 from main text)

Hirshfeld surface analysis is an established method to illustrate differences in intermolecular interactions between molecules and is especially useful for analyzing polymorphic structures. **Figures 5, 6,** and **7** show the front and back of the d_{norm} Hirshfeld surface for **1a, 1b**, and **1c**, respectively. The "front" face of each molecule is the one that contains μ_3-Cl4 while the "back" face is the one that contains μ_3-Cl5. Although **1a** is the densest polymorph, the Hirshfeld surface of **1b** has the largest number of significant interactions. The latter is also the only polymorph that exhibits interactions between dianionic complexes, while the **1a** and **1c** only have surface interactions with the tetrabutylammonium cations.

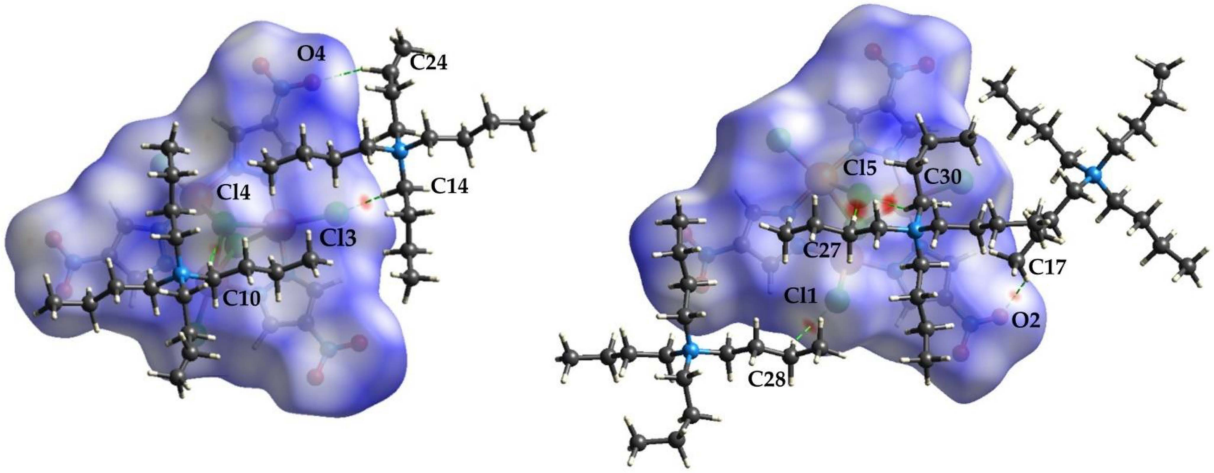


Figure 5. Hirshfeld surface of the front (left) and back (right) of the $[Cu_3(\mu_3\text{-}Cl)_2(\mu\text{-}4\text{-}NO_2\text{-}pz)_3Cl_3]^{2-}$ unit of **1a** showing intermolecular interactions with the tetrabutylammonium cations.

Complex **1a** (**Figure 5**) exhibits mainly C – H…Cl interactions and has the strongest interaction with a capping Cl. The front side of the surface shows a weak interaction involving a capping chloride, C10 – H…Cl4 of 3.803(7) Å and a moderate interaction involving a terminal chloride, C14 – H…Cl3 of 3.798(6) Å. There is also a weak interaction between anion and cation, involving one butyl group of the cation and the nitro group of the pyrazolate: C24 – H…O4 of

3.534(13) Å. The back side of the surface shows two strong interactions of butyl groups with the capping chloride (Cl5): C27 – H…Cl5 (3.689(5) Å) and C30 – H…Cl5 of 3.651(4) Å, along with a moderate interaction involving a terminal chloride, C28 – H…Cl1 of 3.610(6) Å. Another moderate interaction is seen involving the nitro group of the pyrazolate, C17 – H…O2 (3.36(1) Å). In total, the Cu complex is in contact with five different tetrabutylammonium cations.

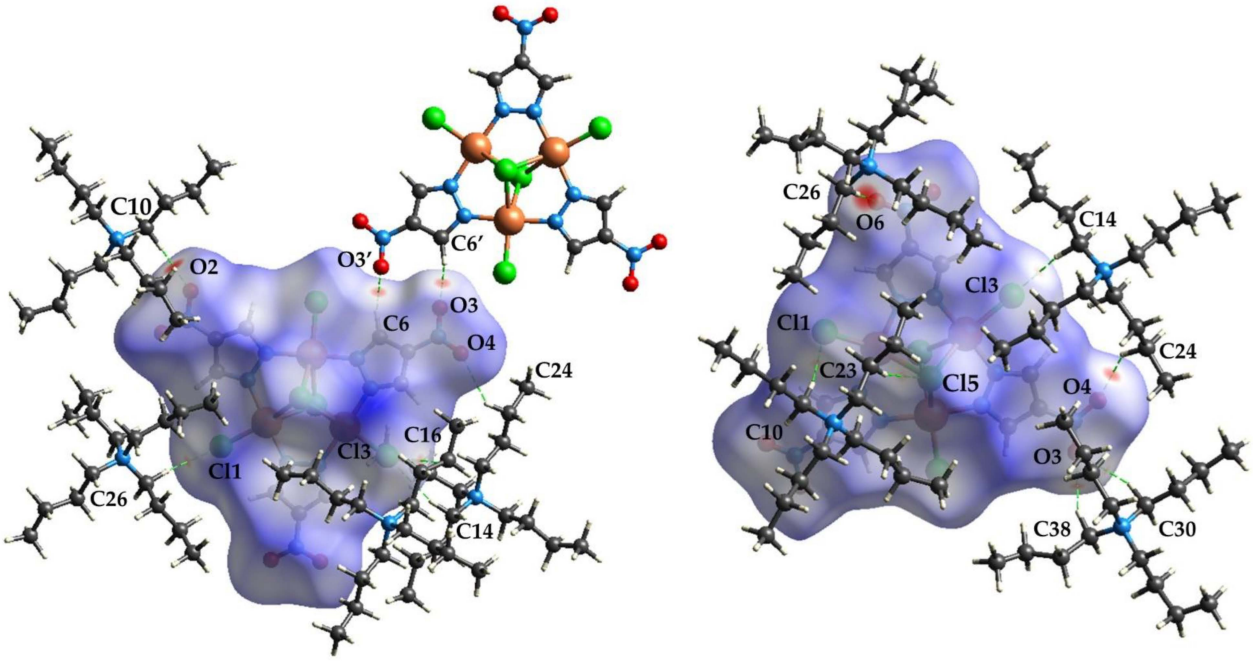


Figure 6. Hirshfeld surface of the front (left) and back (right) of the $[Cu_3(\mu_3\text{-}Cl)_2(\mu\text{-}4\text{-}NO_2\text{-}pz)_3Cl_3]^{2-}$ unit of **1b** showing intermolecular interactions with the tetrabutylammonium cations and other Cu_3 dianionic complexes.

Complex **1b** (**Figure 6**) exhibits the most significant Hirshfeld surface interactions, the strongest of which involve the nitro group. There are a few interactions with both terminal and capping chloride ligands, however, they are much weaker than those of **1a**. From the front of the surface, a strong interaction between C10 – H…O2 of 3.404(8) Å can be seen. The next strongest interaction is between the 4-NO_2-pyrazoles of two separate Cu complexes: O3…H – C6' and the reciprocal O3'…H – C6 of 3.271(7) Å. Weak interactions exist involving the terminal chlorides: C26 – H…Cl1 (3.822(6) Å), C16 – H…Cl3 (3.629(4) Å) and C14 – H…Cl3 (3.829(4) Å). The back of the molecule shows two strong interactions and two weak interactions involving the nitro groups of two pyrazolates: C26 – H…O6 (3.375(8) Å), C24 – H…O4 (3.356(9) Å), C38 – H…O3 (3.520(6) Å), and C30 – H…O3 (3.570(6) Å). There is also a weak interaction involving a terminal chloride: C10 – H…Cl1 (3.838(4) Å). Polymorph **1b** is also the only one in which cations wrap around the complex and display interactions with both the front and back of the surface. Overall, the surface has interactions with seven different cations and one Cu_3 complex.

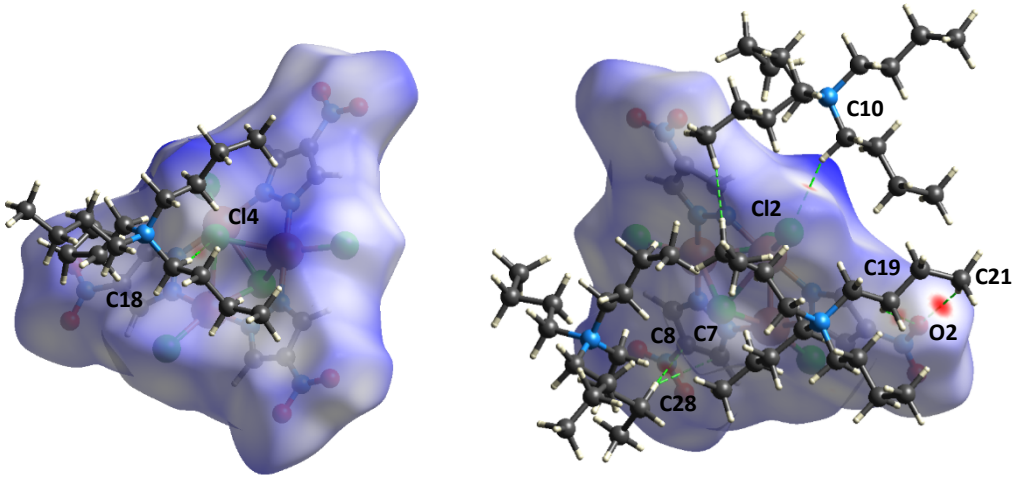


Figure 7. Hirshfeld surface of the front (left) and back (right) of the $[Cu_3(\mu_3\text{-}Cl)_2(\mu\text{-}4\text{-}NO_2\text{-}pz)_3Cl_3]^{2-}$ unit of **1c** showing intermolecular interactions with the tetrabutylammonium cations.

The surface of **1c** (**Figure 7**) exhibits the least amount of interactions, only having significant ones with four cations in total. The front of the surface displays a weak interaction involving the capping chloride (μ_3-Cl4): C18 – H…Cl4 (3.825(9) Å). The back of the surface shows a strong interaction involving the pyrazolate nitro group: C21 – H…O2 (3.36(2) Å). There is also a moderate interaction involving the terminal chloride: C10 – H…Cl2: (3.764(11) Å). The last weak interaction from the surface of **1c** is between a tetrabutylammonium cation and the pyrazolate ring: C28 – H…C7/C8 (3.72(3) Å).