

Article

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

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Abstract: The crystal structure of the ferromagnetically-coupled Cu^{II}₃–pyrazolato complex, (Bu₄N)₂[Cu₃(μ₃-Cl)₂(μ-4-NO₂-pz)₃Cl₃] (**1a**, pz = pyrazolato anion), was originally determined in the triclinic *P*-1 space group. By varying the recrystallization solvent and temperature, two additional true polymorphs were crystallized in the monoclinic *P*₂₁/*n* (**1b**) and orthorhombic *Pbca* (**1c**) space groups. Comparison of the metric parameters of the three polymorphs revealed only minor variations in their bond lengths and angles but clearly distinguishable packing patterns. The DFT calculations showed that, in vacuum, **1a** had the lowest energetic minimum (also the densest of three polymorphs), whereas **1b** and **1c** lay at 6.9 kcal/mol and 7.8 kcal/mol higher energies. The existence of isolable **1b** and **1c** is, therefore, attributed to the intermolecular interactions analyzed by the Hirshfeld methods.

Keywords: polymorphism; Hirshfeld analysis; DFT calculations; trinuclear copper; pyrazolato ligands



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1. Introduction

Polymorphism [1] is a well-established phenomenon in organic compounds, resulting in the manifestation of critical differences in the pharmaceutical properties of compounds crystallized as different polymorphs [2,3]. Polymorphism is also common among minerals—calcium carbonate and the 14 known polymorphs of silica are good examples—and binary or ternary solid-state materials with often strikingly different properties manifested by their various forms [4,5]. Metal organic frameworks (MOFs) are also commonly encountered [6], as are materials undergoing a phase transition to a new polymorph under pressure. In contrast, transition metal complexes are rarely encountered as true polymorphs at ambient conditions [7–11]; a few more examples were included in a review article [12].

Trinuclear copper pyrazolato complexes of the general formula, [Cu₃(μ₃-E)(μ-4-R-pz)₃X₃]^z, where E = OH, O, (Cl)₂, (Br)₂, and OMe; R = H, Cl, Br, I, Me, NO₂, -CHO, and -COOEt; X = Cl, Br, PhCOO-, py, SCN-, and MeCOO-, and z = 2-, 1-, and 2+, have been studied in our laboratory for over two decades for their interesting magnetic, structural, and electrochemical properties [13–21]. The capping ligand E forces the Cu₃E motif into one of three geometries: planar (Cu₃O), trigonal pyramidal (Cu₃(OH)), or trigonal bipyramidal (Cu₃X₂).

We have previously published a ferromagnetically coupled Cu^{II}₃–pyrazolato complex, (Bu₄N)₂[Cu₃(μ₃-Cl)₂(μ-4-NO₂-pz)₃Cl₃] (**1a**), which crystallized in the triclinic *P*-1 space group [22]. Herein, we report its two true polymorphs in the *P*₂₁/*n* (**1b**) and *Pbca* (**1c**) space groups and discuss the analyses of their Hirshfeld surfaces and energies calculated by DFT methods.

2. Materials and Methods

2.1. Materials

All reagents, except 4-nitro-pyrazole were purchased from commercial sources and used as received. 4-Nitro-pyrazole was synthesized following procedures in the literature [23]. The solvents were purified and dried using standard techniques [24].

2.2. Synthesis

The synthetic method for $(\text{Bu}_4\text{N})_2[\text{Cu}_3(\mu_3\text{-Cl})_2(\mu\text{-4-NO}_2\text{-pz})_3\text{Cl}_3]$ has been previously published along with the crystal structure of **1a** [22]. Whereas the trinuclear complex was synthesized in the manner reported, the crystallization of **1a–c** differed as follows: saturated solutions of the complex in boiling n-propyl alcohol (**1a**), n-butyl alcohol (**1b**), and methanol (**1c**) were filtered while hot and allowed to cool down under ambient conditions, resulting in X-ray quality crystals. Except for the methanol, a small amount of acetonitrile was added to the alcoholic solution during crystallization to prevent the formation of oily products on cooling.

2.3. X-ray Crystallography and Data Collection

X-ray diffraction data were collected with a Bruker AXS SMART 1K CCD diffractometer [25] with graphite-monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) at ambient temperature. The data were corrected for Lorentz and polarization effects [26]. The structures were solved using the SHELXTL-direct methods program, then refined by full-matrix least squares methods on F^2 [27]. The crystal data and structure refinement parameters are listed in Table 1. CCDC 2215557 (**1b**) and 2215558 (**1c**) contain the supplementary crystallographic data for this paper and can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Table 1. Crystal data and structure refinement parameters for **1a–c**.

	1a [22]	1b	1c
Formula	$\text{C}_{41}\text{H}_{78}\text{Cl}_5\text{Cu}_3\text{N}_{11}\text{O}_6$	$\text{C}_{41}\text{H}_{78}\text{Cl}_5\text{Cu}_3\text{N}_{11}\text{O}_6$	$\text{C}_{41}\text{H}_{78}\text{Cl}_5\text{Cu}_3\text{N}_{11}\text{O}_6$
Formula Weight	1189.01	1189.01	1189.01
Temperature (K)	299(2)	298(2)	298(2)
Crystal System	Triclinic	Monoclinic	Orthorhombic
Space Group	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)	$Pbca$ (No. 61)
$a/\text{\AA}$	13.121(1)	15.526(2)	21.944(2)
$b/\text{\AA}$	15.183(1)	20.938(3)	15.783(2)
$c/\text{\AA}$	15.625(1)	18.904(3)	33.886(4)
$\alpha/^\circ$	108.778(2)	90	90
$\beta/^\circ$	102.082(2)	108.746(2)	90
$\gamma/^\circ$	95.916(2)	90	90
$V/\text{\AA}^3$	2832.5(5)	5819(1)	11,736(2)
Z	2	4	8
$D_{\text{calc}}/\text{g cm}^{-3}$	1.394	1.357	1.346
μ/mm^{-1}	1.402	1.365	1.354
Refl. Collected	12,635	30,317	62,961
Unique Refl.	8156	10,274	10,358
Obs. Refl. ($I > 2\sigma(I)$)	4654	6065	4571
θ range/ $^\circ$	1.42–23.30	1.50–25.03	1.20–25.04
Data	8156	10,274	10,358
Restraints/param.	0/603	0/603	6/603
$R(F)$; $R_w(F)$ ($I > 2\sigma(I)$)	0.0401; 0.0914	0.0476; 0.1294	0.0795; 0.2176
GooF	0.914	1.000	1.003

2.4. DFT Calculations

DFT calculations were carried out, with geometry optimization, without symmetry restrictions using the B3LYP [28,29] hybrid density functional with the 6-31G* basis set for all atoms [30] using Gaussian-09 [31] software. Correctness of the calculated electronic states was ensured by checking the stability of the SCF solutions; the calculations confirmed that all the considered structures had the quartet ground electronic state. Geometry optimizations were carried out in the gas phase.

2.5. Software

Geometric calculations and visual representations of the molecules were obtained from both *Olex2* [32] and *Mercury 2020.3.0* [33]. Hirshfeld surfaces, fingerprint plots, and the associated images were calculated and obtained using *CrystalExplorer17* [34]. Hirshfeld surface analysis and the capabilities of *CrystalExplorer* are well discussed in the literature [35–38].

3. Results and Discussion

3.1. Crystal Structure Descriptions

3.1.1. General Structure Description

A representative structure of the $[\text{Cu}_3(\mu_3\text{-Cl})_2(\mu\text{-4-NO}_2\text{-pz})_3\text{Cl}_3]^{2-}$ unit of **1a**, **1b**, and **1c** is shown in Figure 1, and selected bond lengths of each polymorph are listed in Table 2. The charge in each dianionic complex is balanced by two crystallographically independent tetrabutylammonium cations. **1a** was previously crystallized from boiling n-propyl alcohol and reported in the *P*-1 space group, while **1b** was crystallized from boiling n-butyl alcohol in the *P*₂₁/*n* space group, and **1c** was crystallized from boiling methanol in the *Pbca* space group. As the symmetry of each polymorph increased from the triclinic to monoclinic to orthorhombic crystal systems, the crystal density (as reported in Table 1) decreased from 1.394 g cm^{−3} to 1.357 g cm^{−3} to 1.346 g cm^{−3}.

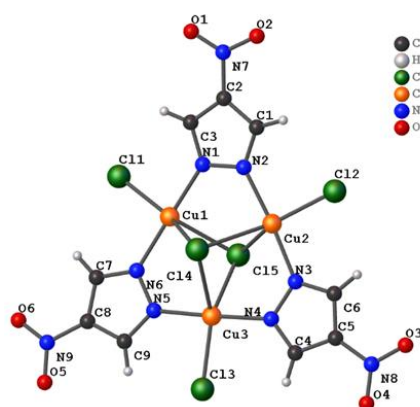


Figure 1. Representative structure and atom numbering scheme of the $[\text{Cu}_3(\mu_3\text{-Cl})_2(\mu\text{-4-NO}_2\text{-pz})_3\text{Cl}_3]^{2-}$ unit for **1(a–c)**.

Table 2. Selected bond lengths (Å) for **1a–1c**.

	1a	1b	1c
Cu1–Cl1	2.234(2)	2.275(1)	2.256(2)
Cu1–Cl4	2.501(2)	2.659(1)	2.680(3)
Cu1–Cl5	2.628(1)	2.510(1)	2.480(2)
Cu1–N1	1.939(4)	1.948(4)	1.950(6)
Cu1–N6	1.950(4)	1.944(3)	1.942(6)
Cu2–Cl2	2.255(2)	2.232(1)	2.267(2)
Cu2–Cl4	2.558(1)	2.594(1)	2.679(2)
Cu2–Cl5	2.614(2)	2.560(1)	2.490(2)
Cu2–N2	1.947(4)	1.950(4)	1.937(6)
Cu2–N3	1.946(4)	1.951(3)	1.926(7)
Cu3–Cl3	2.276(2)	2.271(1)	2.255(3)
Cu3–Cl4	2.584(2)	2.513(1)	2.465(2)
Cu3–Cl5	2.501(1)	2.615(1)	2.642(2)
Cu3–N4	1.960(4)	1.945(3)	1.964(7)
Cu3–N5	1.966(4)	1.953(3)	1.950(7)
Cu1 ... Cu2	3.381(1)	3.419(9)	3.420(2)
Cu1 ... Cu3	3.389(1)	3.404(8)	3.386(2)
Cu2 ... Cu3	3.433(1)	3.397(1)	3.423(2)

3.1.2. Tau Parameter Determination

In all cases, the Cu centers are in a triangular arrangement and the 5-coordinate environment of each Cu atom is formed by two μ -4-NO₂-pyrazolate bridges, two μ_3 -Cl caps, and one terminal Cl ligand. While the Cu-N bond lengths of each [Cu₃(μ_3 -Cl)₂(μ -4-NO₂-pz)₃Cl₃]^{2−} unit are the same within experimental error, each polymorph exhibits different ligand (chloride and pyrazolate) positions in relation to the Cu₃-plane and different Cu-Cl bond lengths. The geometry of 5-coordinate metal centers can be ideally represented as either square-pyramidal (trans angles $\alpha = \beta = 180^\circ$) or trigonal bipyramidal ($\alpha = 120^\circ$; $\beta = 180^\circ$) where β is the largest angle and α is the second largest. For complexes that deviate from ideal geometries, the τ parameter, defined as follows, provides a quantitative description of the coordination geometry [39]:

$$\tau = \frac{(\beta - \alpha)}{60} \quad (1)$$

Therefore, $\tau = 0$ for a perfectly square pyramidal complex, and $\tau = 1$ for a perfectly trigonal bipyramidal complex. The tau parameters calculated for each one of the three Cu-centers of the polymorphs, along with the total deviation of the three Cu-centers of each polymorph, $\Sigma\tau$, are listed in Table 3.

Table 3. Selected bond angles ($^\circ$) and calculated τ values for **1a–1c**.

		1a		1b		1c	
Cu1	$\angle 1$	Cl1-Cu1-Cl5	119.56	Cl1-Cu1-Cl5	132.23	Cl1-Cu1-Cl5	163.74
	$\angle 2$	Cl1-Cu1-Cl4	160.39	Cl1-Cu1-Cl4	147.74	Cl1-Cu1-Cl4	116.35
	$\angle 3$	Cl4-Cu1-Cl5	79.99	Cl4-Cu1-Cl5	80.03	Cl4-Cu1-Cl5	79.89
	$\angle 4$	N1-Cu1-N6	173.43	N1-Cu1-N6	172.60	N1-Cu1-N6	176.43
	τ	$(\angle 4 - \angle 2)/60$	0.22	$(\angle 4 - \angle 2)/60$	0.41	$(\angle 4 - \angle 1)/60$	0.21
Cu2	$\angle 1$	Cl2-Cu2-Cl5	120.58	Cl1-Cu1-Cl5	132.23	Cl2-Cu2-Cl5	133.70
	$\angle 2$	Cl2-Cu2-Cl4	160.14	Cl1-Cu1-Cl4	147.74	Cl2-Cu2-Cl4	146.56
	$\angle 3$	Cl4-Cu2-Cl5	79.24	Cl4-Cu1-Cl5	80.03	Cl4-Cu2-Cl5	79.73
	$\angle 4$	N2-Cu2-N3	173.32	N1-Cu1-N6	172.60	N2-Cu2-N3	172.86
	τ	$(\angle 4 - \angle 2)/60$	0.22	$(\angle 4 - \angle 2)/60$	0.54	$(\angle 4 - \angle 2)/60$	0.44
Cu3	$\angle 1$	Cl3-Cu3-Cl5	138.45	Cl1-Cu1-Cl5	132.23	Cl3-Cu3-Cl5	130.39
	$\angle 2$	Cl3-Cu3-Cl4	140.69	Cl1-Cu1-Cl4	147.74	Cl3-Cu3-Cl4	148.69
	$\angle 3$	Cl4-Cu3-Cl5	80.85	Cl4-Cu1-Cl5	80.03	Cl4-Cu3-Cl5	80.90
	$\angle 4$	N4-Cu3-N5	174.94	N1-Cu1-N6	172.60	N4-Cu3-N5	174.36
	τ	$(\angle 4 - \angle 2)/60$	0.57	$(\angle 4 - \angle 1)/60$	0.51	$(\angle 4 - \angle 2)/60$	0.43
$\Sigma\tau$		1.01		1.46		1.08	

The tau parameters for complex **1b** are most consistently between square pyramidal and trigonal bipyramidal. The highest tau value of 0.57 is encountered for the Cu3 of **1a**, while the lowest one of 0.21 is for the Cu1 of **1c**; thus, the geometries of these two metal centers better adheres to the trigonal bipyramidal and square pyramidal, respectively. However, the higher total deviation of the three Cu-centers is encountered in **1b**. Figure 2 illustrates the differences in the geometries of these two extremes. For each case, the copper atom and immediate coordination sphere are shown in two different orientations: (1) Cl4 as the axial ligand (square pyramidal) and (2) the nitrogen atoms as the axial ligands (trigonal bipyramidal).

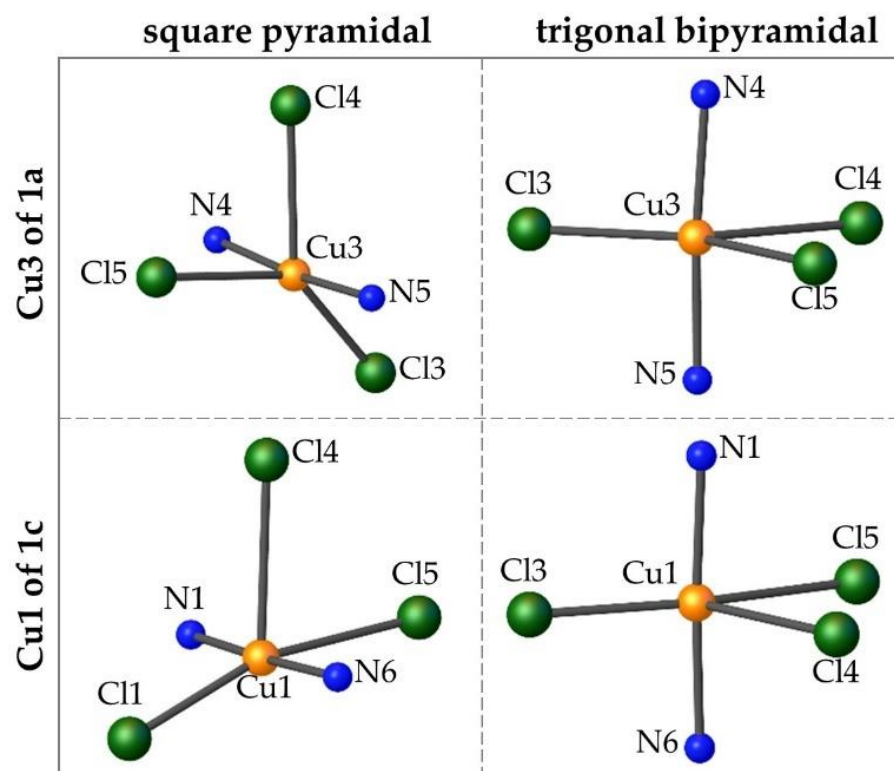


Figure 2. Comparison of the square pyramidal and trigonal bipyramidal geometries for the Cu3 of **1a** ($\tau = 0.57$) and the Cu1 of **1c** ($\tau = 0.21$).

3.1.3. Ligand Position in Relation to the Cu₃ Plane

Another illustrative parameter for describing the three polymorphs is the distance of the three terminal chloride atoms and the three 4-NO₂-pyrazolate ligands from the Cu₃-plane, as reported in Table 4. Here, a centroid was calculated for each pyrazolate ring: pz1 refers to the centroid of the plane that contains N1, N2, C1, C2, and C3; pz2 refers to the centroid of the plane that contains N3, N4, C4, C5, and C6; and pz3 refers to the centroid of the plane that contains N5, N6, C7, C8, and C9. A positive or negative sign is attributed to the ligand being either above or below the Cu-plane, respectively, with each molecule oriented so that Cl5 is above the plane and Cl4 is below the plane.

Table 4. Distances (d, Å) of the terminal chloride ligands and pyrazolates from the Cu₃-plane for **1a–c**.

	Cl1	Cl2	Cl3	$ \Sigma_{d_{Cl}} $	$\Sigma_{ \Sigma_{d_{Cl}} }$	pz1	pz2	pz3	$ \Sigma_{d_{pz}} $	$\Sigma_{ \Sigma_{d_{pz}} }$
1a	0.799	0.758	−0.017	1.540	1.574	−0.278	−0.133	−0.075	0.486	0.486
1b	−0.275	−0.116	0.150	0.241	0.541	0.427	−0.145	0.013	0.295	0.585
1c	0.912	−0.248	−0.486	0.178	1.646	0.276	0.018	−0.302	0.008	0.596

Due to the bridging nature of the pyrazolates, the distance between the terminal Cl ligands and the Cu₃-plane is larger than that of the pyrazolate rings (as expected) except for **1b**—in which $|\Sigma_{d_{pz}}|$ and $\Sigma_{|\Sigma_{d_{pz}}|}$ are larger by 0.054 and 0.044, respectively. **1c** has the largest values for both $\Sigma_{|\Sigma_{d_{Cl}}|}$ and $\Sigma_{|\Sigma_{d_{pz}}|}$, therefore, exhibiting the most deviation either above or below the Cu₃-plane. However, when the sum is calculated, allowing for the total effect to be taken into consideration— $|\Sigma_{d_{Cl}}|$ and $|\Sigma_{d_{pz}}|$ —, **1c** has the smallest values of the three polymorphs.

3.1.4. Crystal Packing

As the name suggests, the three polymorphs give rise to vastly different crystal packing motifs. The types of interactions that dominate each polymorph are discussed more in depth in Section 3.3 (*vide infra*). For simplicity, the crystal packing of the complex is shown separately from that of the cations. The crystal packing viewed parallel to the Cu_3 plane for each molecule is shown in Figure 3. The complexes of **1a** are arranged in pairs that exhibit repulsions between a terminal chloride (Cl2) and the nitro group of a pyrazolate. The $\text{Cl2} \dots \text{N7}$ distance is 3.660 Å. These pairs of cations are eclipsed and extend down the *a*-axis. The complexes of **1b** are arranged in a manner that allows for the nitro groups of pyrazolates to be stacked with a $\text{N7} \dots \text{N7}$ distance of 3.246 Å. Two other pyrazolates have reciprocal $\text{C-H} \dots \text{O}$ interactions with a $\text{C6} \dots \text{O3}$ distance of 3.271 Å. These two types of pyrazolate interactions alternate parallel to the *b*-axis. The complexes of **1c** are arranged in pairs with one nitro group (O1-N7-O2) having interactions with a terminal and capping chloride. The $\text{N7} \dots \text{Cl1}$ distance is 3.767 Å with the chloride ligand bending away from the nitro group. The $\text{O1} \dots \text{Cl5}$ distance is 3.432 Å. Unlike the pairs in **1a**, the pairs in **1c** do not extend into the plane; instead, they rotate $\sim 90^\circ$ down the plane shown in Figure 3.

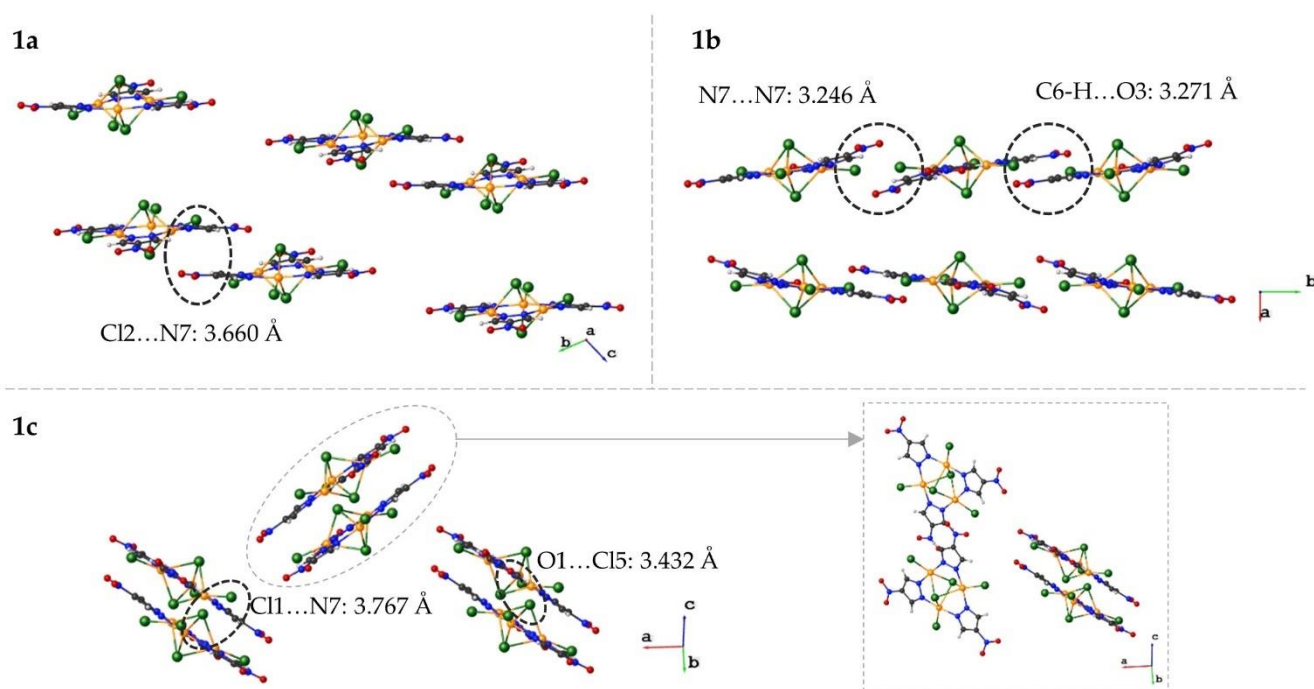


Figure 3. Crystal packing of the dianionic complex viewed approximately parallel to the Cu_3 plane for **1a** (top left), **1b** (top right), and **1c** (bottom). The inset of **1c** shows the rotation of the pair directly behind and in front of the specified pair. Significant interactions are circled and labeled with the identity and distance of the interaction.

The crystal packing of the tetrabutylammonium cations for each molecule are shown in Figure 4. In each polymorph, layers of chains are formed. In **1a**, the chains are approximately linear, running alternately parallel to the *b*-axis and diagonally in the *bc* plane. The dianionic copper complexes occupy the spaces formed between the diagonal cation chains. The cations in **1b** form sinusoidal waves that propagate parallel to the *c*-axis; the adjacent layers of cation waves are out of phase. The complex anions occupy the channels created by layers of waves. The cations in **1c** form corrugated layers parallel to the *a*-axis. Between consecutive layers are pairs of crystallographically non-independent cations. Four complex molecules surround each pair of cations between the layers.

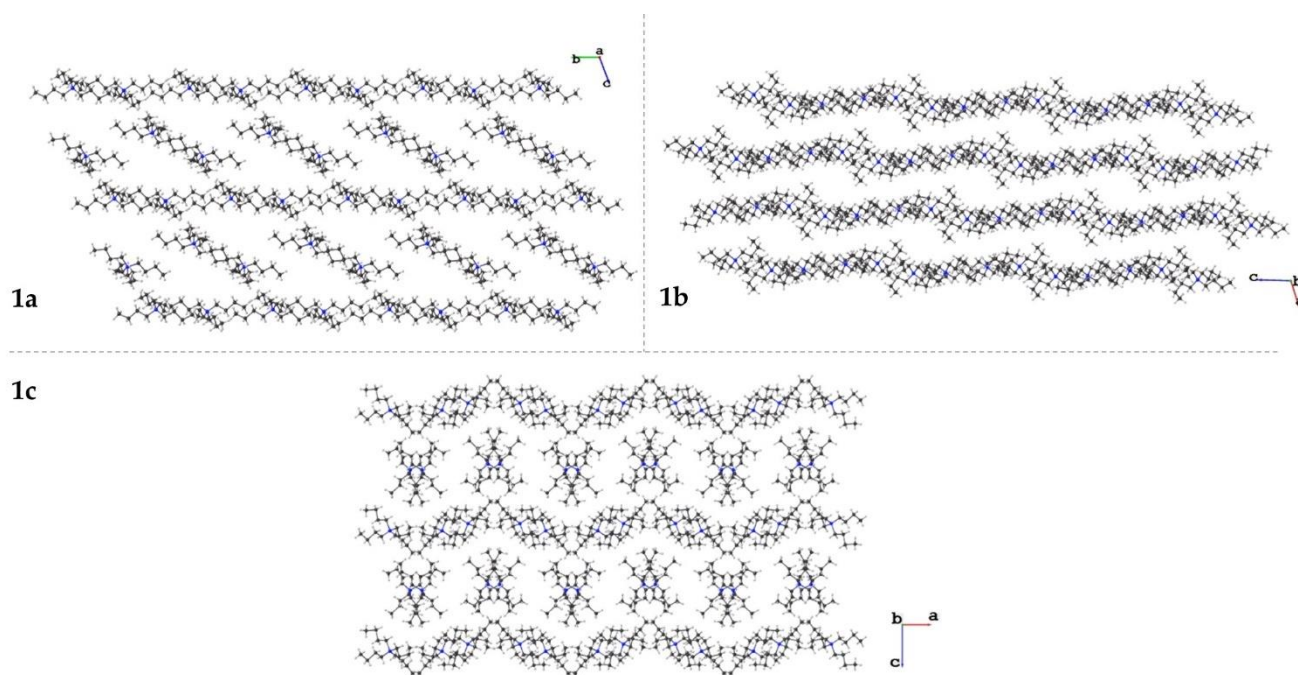


Figure 4. Crystal packing of the two crystallographically independent tetrabutylammonium cations for **1a** (top left), **1b** (top right), and **1c** (bottom).

3.2. DFT Calculations

The potential energies of the three polymorphs were calculated in the gas phase at the B3LYP/6-31G* level of theory. Since calculations of vibrational frequencies were not feasible for molecules of this size, zero-point vibrational energy corrections were not considered. However, this is not expected to affect the computed relative energies significantly. According to the calculations, all three structures correspond to the local minima at the potential energy surface, with **1a** having the lowest energy, and **1b** and **1c** lying respectively 6.9 and 7.8 kcal/mol higher; these results should be interpreted qualitatively, because their differences are within the range of B3LYP accuracy. The main structural difference in the gas phase is the position of the tetrabutylammonium cations with respect to the central $\text{Cu}_3(\mu_3\text{-Cl})_2(\mu\text{-4-NO}_2\text{-pz})_3\text{Cl}_3$ anion, which is diagonal in **1a**, horizontal in **1b**, and vertical in **1c**.

3.3. Hirshfeld Surface Analysis

Figures 5–7 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 $\mu_3\text{-Cl4}$ while the “back” face is the one that contains $\mu_3\text{-Cl5}$. Although **1a** is the densest polymorph, the Hirshfeld surface of **1b** has the largest number of significant interactions. In total, the Cu complexes of **1a**, **1b**, and **1c** are in contact with five, seven, and four different tetrabutylammonium cations, respectively. In addition, the surface of **1b** has significant interactions with one dianionic complex, while **1a** and **1c** do not exhibit complex–complex interactions. The types of complex–cation interactions that dominate each polymorph differ as follows. **1a** exhibits mainly C–H ... Cl interactions and has two strong interactions with a capping Cl (C27–H ... Cl5 (3.689(5) Å) and C30–H ... Cl5 of 3.651(4) Å). **1b** exhibits the strongest interactions involving the nitro group of the pyrazolate ligands (C24–H ... O4 (3.356(9) Å), C26–H ... O6 (3.375(8) Å), C10–H ... O2 (3.404(8) Å, C38–H ... O3 (3.520(6) Å), and C30–H ... O3 (3.570(6) Å). **1b** also has an interaction between the 4-NO₂-pyrazolates of two separate Cu complexes: O3 ... H–C6' and the reciprocal O3' ... H–C6 of 3.271(7) Å. **1c** also has its strongest interaction with the nitro group of a pyrazolate (C21–H ... O2 (3.36(2) Å) and is the only polymorph to have an interaction with the ring of the 4-NO₂-

pyrazolate (C28-H ... C7/C8 (3.72(3) Å). A more in-depth description of the Hirshfeld surface interactions can be found in the supplemental information.

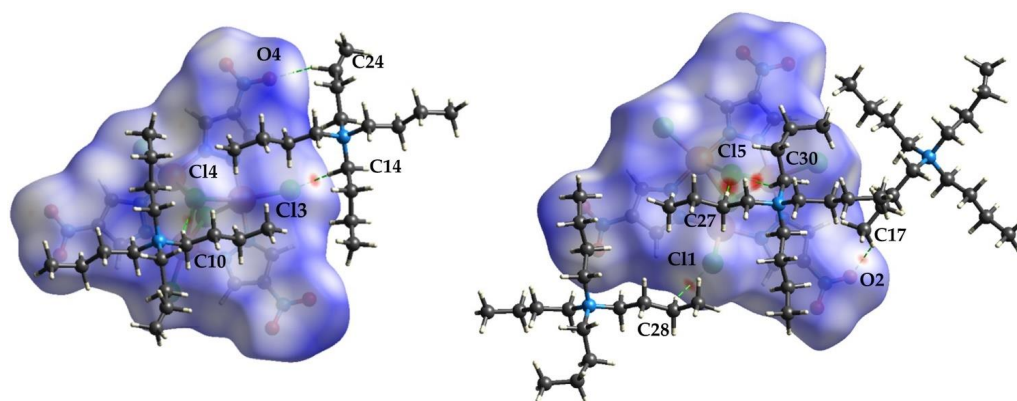


Figure 5. Hirshfeld surface of the front (**left**) and back (**right**) of the $[\text{Cu}_3(\mu_3\text{-Cl})_2(\mu\text{-4-NO}_2\text{-pz})_3\text{Cl}_3]^{2-}$ unit of **1a** showing the intermolecular interactions with the tetrabutylammonium cations.

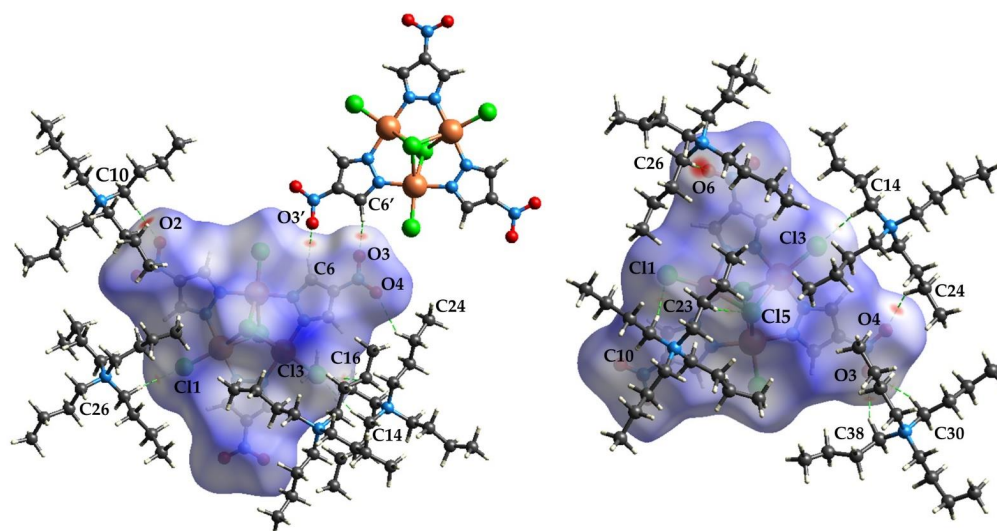


Figure 6. Hirshfeld surface of the front (**left**) and back (**right**) of the $[\text{Cu}_3(\mu_3\text{-Cl})_2(\mu\text{-4-NO}_2\text{-pz})_3\text{Cl}_3]^{2-}$ unit of **1b** showing the intermolecular interactions with the tetrabutylammonium cations and other Cu_3 dianionic complexes.

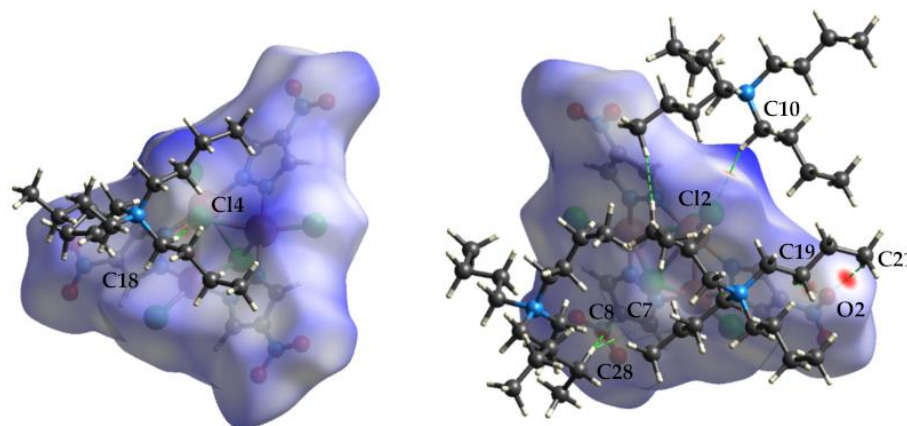


Figure 7. Hirshfeld surface of the front (**left**) and back (**right**) of the $[\text{Cu}_3(\mu_3\text{-Cl})_2(\mu\text{-4-NO}_2\text{-pz})_3\text{Cl}_3]^{2-}$ unit of **1c** showing the intermolecular interactions with the tetrabutylammonium cations.

From the d_{norm} Hirshfeld surfaces, 2D fingerprint plots were assembled as shown in Figure 8. All three polymorphs show the most interactions (dark blue = small number of interactions, while green = moderate number of interactions) around $d_i \approx 2 \text{ \AA}$, $d_e \approx 1.4 \text{ \AA}$. The main difference between the shape of each plot is the number of interactions at high d_i/d_e values. **1a** is the densest polymorph, and thus its surface has fewer long-range interactions (those above $d_i \approx d_e \approx 2.6 \text{ \AA}$). The other main difference is the number of spikes of each fingerprint plot. **1a** has two main spikes. The first is located roughly at $d_i \approx 1.4 \text{ \AA}$, $d_e \approx 1.1 \text{ \AA}$ and continues diagonally upwards. This depicts the O...H interactions. The second spike is located roughly at $d_i \approx 1.6 \text{ \AA}$, $d_e \approx 1.0 \text{ \AA}$ and continues diagonally upwards. This spike is attributed to the Cl...H interactions. **1b** has the highest number of spikes (four) of the polymorphs: (1) $d_i \approx 1.1 \text{ \AA}$, $d_e \approx 1.4 \text{ \AA}$; (2) $d_i \approx d_e \approx 1.2 \text{ \AA}$; (3) $d_i \approx 1.3 \text{ \AA}$, $d_e \approx 1.0 \text{ \AA}$; and (4) $d_i \approx 1.7 \text{ \AA}$, $d_e \approx 1.1 \text{ \AA}$. The O...H interactions account for the first and third spikes. The second spike is attributed to the H...H interactions, and the fourth spike is attributed to the Cl...H interactions. The Cl...H interactions of **1b** are not as strong as those of **1a**; however, the O...H interactions of **1b** are stronger than those of **1a**. The plot of **1c** shows three spikes: (1) $d_i \approx d_e \approx 1.1 \text{ \AA}$; (2) $d_i \approx 1.4 \text{ \AA}$, $d_e \approx 1.0 \text{ \AA}$; and (3) $d_i \approx 1.7 \text{ \AA}$, $d_e \approx 1.1 \text{ \AA}$. These are attributed to the H...H, O...H, and Cl...H interactions, respectively. Here, the H...H interactions are slightly stronger than in **1b**, while the strength of the O...H interactions is similar to **1a**, and the strength of the Cl...H interactions is similar to **1b**. The breakdown of the 2D fingerprint plots by type of atomistic contribution is shown in Figures S1–S3 of the supplementary information.

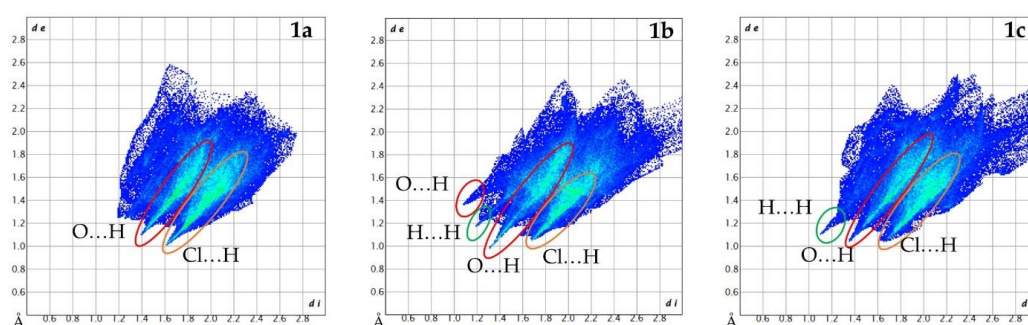


Figure 8. 2D fingerprint plots (d_i/d_e) of **1a** (left), **1b** (middle), and **1c** (right) showing the types of shortest interactions for each Hirshfeld surface.

For all three polymorphs, approximately 93% of all interactions of the complex surface consist of five types: O...H, Cl...H, H...H, C...H, and N...H. There are small differences in the percentages of these interactions, as shown in Figure 9. The remaining interactions account for $\leq 2\%$ of the interactions of each polymorph, and the same type of minor interactions do not occur for each polymorph. For example, **1b** has no Cu...O interactions or Cl...N interactions and is the only polymorph that contains N...N interactions. Only **1a** had Cl...C interactions. **1c** had no O...C interactions.

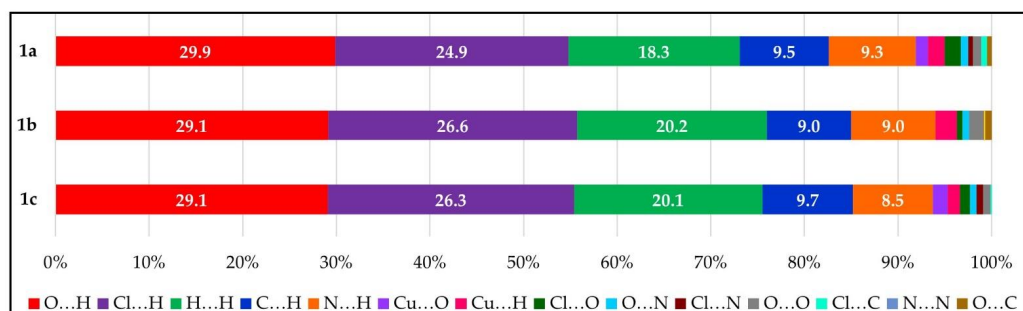


Figure 9. Bar graph, compiling the Hirshfeld surface interactions for **1a–c** analyzed by percent contributions of individual atomic contacts.

4. Conclusions

By varying the crystallization solvent and temperature of $(\text{Bu}_4\text{N})_2[\text{Cu}_3(\mu_3\text{-Cl})_2(\mu\text{-4-NO}_2\text{-pz})_3\text{Cl}_3]$, three true polymorphs of this complex, **1a–c**, have been recognized so far. Aside from the numerous polymorphs of $[\text{M}(\text{acac})_3]$ complexes (where $\text{M} = \text{Fe}$ [40], Cr [41], or Mn [42] and $\text{acac} = \text{acetylacetonate}$), we are aware of only a few other examples of metal complexes known in three polymorphic structures under ambient conditions [7,43]. The X-ray crystal structures of the three polymorphic complexes revealed insignificant variations in their bond lengths and angles in contrast to their clearly differentiated 3D packing and, therefore, differences in intermolecular interactions. The DFT calculations showed that, in vacuum, the triclinic **1a** was the ground state polymorph. However, in the solid state, the sum of the various intermolecular interactions (not quantified here) was significant enough to offset the polymorphic instabilities of 6.9 kcal/mol and 7.8 kcal/mol and allow phase transitions to the monoclinic and orthorhombic forms, **1b** and **1c**, respectively. The intermolecular interactions were qualitatively probed by Hirshfeld surface analysis. Interestingly, **1a** was also the densest, therefore the one with the higher number of contacts involving the $\mu_3\text{-Cl}$, terminal Cl, and NO_2 groups. However, **1b** had the highest number of significant interactions with the Hirshfeld surface, whereas **1c** had only two strong interactions—involving a terminal Cl and a NO_2 group. It was not possible to assess here the role of the crystallization solvent polarity and boiling point.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/cryst12111611/s1>, Figures S1–S3: Breakdown of 2D fingerprint plot by type of individual atomistic contribution for complexes **1a,b**, respectively. Additional Hirshfeld surface analysis of Figures 5–7 in the main text.

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