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A Hirshfeld Surface Analysis, Crystal Structure and Spectroscopic studies of a new Cu(II) halocuprate salt with protonated N-amino-ethyl-piperazine

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Abstract

(C₆H₁₈N₃)₄[CuCl₅]₂[CuCl₄]₃·1.42H₂O has been prepared and characterized by various physicochemical techniques. Single crystal X-ray diffraction structural analysis has revealed that the title compound belongs to the orthorhombic system with space group *Cmca*. Its unit cell dimensions are: *a* = 24.286 (2) Å, *b* = 14.3082 (14) Å, *c* = 16.6160 (16) Å, with *Z* = 4, *V* = 5773.8 (10) Å³ and its crystal structure was determined and refined down to *R* = 0.024 and *wR* (*F*²) = 0.059. The structure contains three crystallographically independent Cu²⁺ ions coordinated to chlorine anions in various fashions. Cu1 is five-coordinated, in a distorted square pyramidal fashion, while Cu2 and Cu3 are tetra-coordinated in square planar and distorted tetrahedral fashions, respectively. The entities are interconnected by means of hydrogen bonding [O(W)-H...Cl, N-H...Cl, C-H...Cl and C-H...O(W)] forming a three-dimensional network. Intermolecular interactions were investigated by Hirshfeld surfaces and the contacts of the eight different chloride atoms were notably compared. The vibrational absorption bands were identified by infrared spectroscopy. The optical study was investigated by UV–vis absorption.

Keywords: Organic-inorganic hybrid material; Cu(II) complex; X-ray diffraction; Coordination compound; Hirshfeld surface; Infrared and Ultraviolet-visible (UV-vis) spectroscopy.

1. Introduction

The coordination compounds of metal halides have been interesting due to their unique structural features, for their rich photo-luminescent, magnetic properties, ferroelectric, electronic and interesting optical properties [1 - 17]. Among these compounds, transition metal complexes, especially Cu(II) complexes, are known to be effective against rheumatoid arthritis and they also show anti-ulcer activity [18, 19]. The Cu(II) complexes have different molecular geometries, such as tetrahedral, square planar, square pyramidal and octahedral [20].

One of the best studied groups of copper complexes, both in solution and the solid state, are the halocuprate complexes [21, 22]. The presence of an active Jahn-Teller effect in the d⁹ electronic system and the relative flatness of the potential energy surfaces lead to a pronounced plasticity of the metal coordination sphere with a large structural variability and great variety of crystalline architectures with different coordination numbers, geometries, nuclearities and cluster sizes. The halocuprates and their properties are of interest not only in inorganic chemistry but also in fields ranging from solid-state physics to bioinorganic chemistry. Their diversity and ability to easily interconvert into each other make these systems excellent

candidates for analyzing correlations between structural parameters and magnetic and optical properties [23, 24].

2. Experimental

2. 1. Chemical preparation

CuCl₂·2H₂O (1 mmol; 0.17 g) was added to an *N*-amino-ethylpiperazine (1 mmol; 0.19 g) solution dissolved in 15 mL of absolute ethanol. The resulting solution was then acidified with 1 mL of concentrated HCl and allowed to evaporate slowly at room temperature. Brown block like crystals of (C₆H₁₈N₃)₄[CuCl₅]₂[CuCl₄]₃·1.42H₂O were formed after 6 days (yield, 87.7%). Anal. Calc.: C, 17.43; H, 4.52; N, 10.17. Found: C, 15.58; H, 4.76; N, 10.31%.

2. 2. Investigation techniques

2. 2. 1. X-ray single crystal structural analysis

Single crystals were carefully selected under a microscope and mounted on a Mitegen micromesh mount with the help of a trace of mineral oil. X-ray diffraction data were collected at 100 K on a Bruker AXS APEXII CCD diffractometer using the ω scan technique with MoK α radiation ($\lambda = 0.7107 \text{ \AA}$). Brown single crystals of the composition (C₆H₁₈N₃)₄[CuCl₅]₂[CuCl₄]₃·1.42H₂O ($M = 1652.17 \text{ g mol}^{-1}$) are orthorhombic: $a = 24.286 (2) \text{ \AA}$, $b = 14.3082 (14) \text{ \AA}$, $c = 16.6160 (16) \text{ \AA}$, $V = 5773.8 (10) \text{ \AA}^3$, space group *Cmca*, $Z = 4$, $D_x (\text{Mg m}^{-3}) = 1.901$, $\mu (\text{MoK}\alpha) = 2.87 \text{ mm}^{-1}$. The intensities of 27813 reflections were measured in the θ range: $2.9^\circ - 32.1^\circ$ for data collection by ω -scanning of a low-quality single crystal of $0.55 \times 0.20 \times 0.04 \text{ mm}^3$ ($R_{\text{int}} = 0.033$). The absorption correction was applied empirically using the Multi-scan procedure. The number of independent and observed [$I > 2\sigma(I)$] reflections are 4890 and 4482 respectively. The data were collected, the unit cell determined, and the data integrated and corrected for absorption and other systematic errors using the Apex2 suite of programs [25]. SHELXS-97 [26] was used to solve the structure using direct methods and SHELXL6.14 [27], SHELXL2014 [28] and SHELXL [29] were used for refinement. The drawings were made with Diamond [30]. The final anisotropic full-matrix least squares resulted in a convergence of the $R [F^2 > 2\sigma(F^2)]$ factor at 0.024, $wR (F^2) = 0.059$, Goodness-of-fit on $F^2 = 1.07$ and $F(000) = 3333$. After the completion of the refinement, the maximum and minimum values of the difference electron density are as follows: $\Delta\rho_{\text{max}} = 0.67 \text{ e \AA}^{-3}$ and $\Delta\rho_{\text{min}}$ is $-0.55 \text{ e \AA}^{-3}$.

A water molecule, located on a twofold axis, is partially occupied. Its H atoms are disordered. The occupancies of the water molecule orientations refined to 0.52(5) and 0.19(5) respectively. Reflection (200) was affected by the beam stop and was omitted from the refinement.

2. 2. 2. Spectroscopic studies

The IR spectrum was recorded in the range $4000 - 400 \text{ cm}^{-1}$ with a “Perkin-Elmer FTIR” spectrophotometer 1000 using samples dispersed in spectroscopically pure KBr pressed into a pellet.

Electronic spectrum was recorded on a Perkin-Elmer Lambda 950 spectrophotometer within the range of $250 - 800 \text{ nm}$.

3. Results and discussion

3. 1. X-ray diffraction study

The structure of the title compound, (C₆H₁₈N₃)₄[CuCl₅]₂[CuCl₄]₃·1.42H₂O, Figure 1, consists of two [CuCl₅]³⁻ and three [CuCl₄]²⁻ discrete anions. All the three *N*-amino-ethylpiperazine nitrogen atoms are protonated. Thus, to ensure charge balance, the structure contains four organic cations. A crystallization water molecule, located on a twofold axis, is partially occupied, and its H atoms are disordered.

The structure contains three crystallographic independent Cu²⁺ ions, Cu1, Cu2 and Cu3. As shown in Fig. 2, Cu1 is coordinated to five chlorine atoms, while Cu2 and Cu3 are surrounded by only four anions. The Cu2 atom, located on a twofold rotation axis, is coordinated in a square planar fashion. The description of the [Cu2Cl₄]²⁻ entity as square planar is justified by the quasi-equivalent Cu2-Cl5 and Cu2-Cl8 bond distances. The Cu-Cl bond lengths fall in the range 2.2676 (5) - 2.3009 (5) Å and the Cl-Cu-Cl bond angles are 90° for *cis* angles and 180° for *trans* angles (Table 1). Analysis of these angles with the τ_4 metric developed by Yang [31] yields a τ_4 value of 0 for Cu2. The τ_4 value is calculated as $\frac{[360 - (\alpha + \beta)]}{141}$; where α and β are two largest angles at the four-coordinate copper(II) atom in question, and the value of zero (0) is indicative of the ideal square-planar geometry, while the value of one (1) indicates ideal tetrahedral geometry. These bond lengths and angles are compatible with the values observed in other homologous derivatives [32 - 34].

Copper atom Cu3 also occupies a special position. The [Cu3Cl₄]²⁻ anion assumes a distorted tetrahedral geometry with *D*_{2h} symmetry, consistent with the anticipated distortions predicted by the Jahn-Teller effect. These distortions are typically measured by the value of the trans Cl-Cu-Cl angle, which is 136.05 (2)° [35]. The observed yellow-orange color of the title compound is also consistent with the value of the *trans* angle [36]. This highly distorted tetrahedral geometry is confirmed by the τ_4 value of 0.69.

The coordination geometry around the Cu1 center is distorted square pyramidal, with five coordinated chlorine ions. The coordination geometry around the Cu1 center is distorted square pyramidal given by a τ value of 0.26 according to Addison's definition ($\tau = 0$, for an ideal square pyramid, and $\tau = 1$, for a perfect trigonal bipyramid) [37].

The shortest Cu...Cu distances are 5.422, 5.947 and 7.717 Å, the intra-molecular Cl...Cl distances are between 3.23 and 4.60 Å in {Cu2Cl₄}, 3.246 and 4.631 Å in {Cu1Cl₅}, 3.435 and 4.155 Å in {Cu3Cl₄} units.

In the structural arrangement, the [Cu3Cl₄]²⁻ anions are located between the corrugated organic chains and connected to them through N-H...Cl and C-H...Cl hydrogen bonds to form layers parallel to the (**b**, **c**) plane (Fig. 3), situated at $x = \frac{(2n+1)}{4}$ (Fig. 4). Within the layers, cavities are created extending along the *b*-axis at (¼, 0, ¼), (¼, 0, ¾), (¾, 0, ¼) and (¾, 0, ¾) (Fig. 4). The crystallization water molecules occupy these cavities through O-H...Cl and C-H...O hydrogen bonds (Fig. 4, Table 2). The {Cu3Cl₄} tetrahedra are interconnected via the H₂O molecules to form chains at $y = \frac{n}{2}$ (Fig. 5). The [Cu2Cl₄]²⁻ and the [Cu1Cl₅]³⁻ anions, located alternately along the *c*-axis direction at $x = \frac{n}{2}$, are inserted between these layers through N-H...Cl and C-H...Cl hydrogen bonds (Fig. 4).

In the title compound, both the hydrogen atoms attached to nitrogen, carbon and oxygen atoms play an important role in formation of extended molecular association through hydrogen bonding, where the Cl and O atoms act as acceptors of hydrogen bonds. Overall, the crystal structure is stabilized via the various types of hydrogen bonding interactions, N-H...Cl, C-H...Cl, C-H...O and O-H...Cl, and the inclusion of a water molecule seems essential for the stabilization of the molecular packing structures. The hydrogen-bonding metrics are summarized in Table 2.

The conformations of piperazindium six-membered rings can be described in terms of Cremer and Pople puckering coordinates [38], i.e., evaluating the parameters *Q* (total puckering amplitude), *q*₂, *q*₃, θ and ϕ . The calculated values for the N1-C1-C2-N2-C4-C3 ring are as follows: *Q* = 0.581 Å, *q*₂ = 0.015 Å, *q*₃ = 0.581 Å, θ = 1.48° and ϕ = -110.28° corresponding to the most stable chair conformation.

3. 2. Hirshfeld surface and enrichment ratio

Analysis of intermolecular interactions using the Hirshfeld surface-based tools represents a major tool to understand the crystal packing [39]. The Hirshfeld surfaces were computed with software MoProViewer [40] around the different independent entities present in the crystal structure. The multiplicity of some atoms in special positions (Cu and Cl⁻) was taken into account in the addition of the different surfaces. The enrichment ratios [41] of the contacts between the different chemical species enable to highlight the contacts that are favored and are likely to be the crystal packing driving force. Hydrogen atoms bound to carbon (Hc) are distinguished from the polar hydrogen atoms bound to oxygen or nitrogen (Hno).

The H and Cl⁻ chemical species contribute to the vast majority of the Hirshfeld surface as both represent more than 40% presence. There are three major contacts with their surface S_{XY} larger than 23%, and globally they constitute more than three quarters of the contact surface: Hc...Cl, Hno...Cl and Cu...Cl. Their enrichment ratios are all larger than unity and are in accordance with their respective strength. The salt bridges Cu²⁺...Cl⁻ are strong electrostatic interactions which are enriched at $E=2.34$ (Table 3), followed by the strong hydrogen bonds Hn/o...Cl⁻. Even the weak H-bonds Hc...Cl⁻ are still favored at $E=1.45$. This suggests that these three major and enriched contacts are the driving force in the crystal packing formation. The nature of the interactions involving the eight independent chloride atoms is illustrated in Figs. 6 and 7. The Cl⁻ anions assume 32%±11% of the surface involved in a salt bridge with Cu²⁺ cations. All Cl⁻ anions interact with the Hc atoms (29±17%). The Cl6 anion is peculiar as it is surrounded by a largely hydrophobic environment reaching 65% of the surface, and does not form any Cl⁻...H-N nor Cl⁻...H-O hydrogen bonds. The 11%±4% of Cl⁻...Cl⁻ contacts are a consequence of the proximity of the chloride atoms that coordinate the two copper atoms.

The Hc...Hc contacts are rare in this crystal and are significantly under-represented with $E=0.50$. The hydrophobic Hc...Hc contacts are disfavored as the organic cations hardly interact with themselves and are mainly surrounded by chlorine atoms. The cations are separated by layers built of anions CuCl_x, which are parallel to the (b, c) plane (Fig. 4). All other self-contacts that involve chemical types with a significant charge (Cl⁻, Cu²⁺, Hn/o^{δ+}, O^{δ-}) are strongly avoided. The copper atom Cu3 is coordinated by only four chloride atoms, the remaining copper surface interacts weakly with the Hc atoms of the cation.

3. 3. IR spectroscopy

To gain more information on the crystal structure, we have undertaken a vibrational study using infrared spectroscopy. The experimental vibrational spectrum is shown in Fig. 8. The assignments of the observed bands are essentially based on comparisons with data previously reported for similar compounds [42, 43].

Heterocyclic compounds containing an N-H group exhibit N-H stretching absorption in the region from 3500 to 3200 cm⁻¹. In the present work, bands between 3520 and 3420 cm⁻¹ are assigned to the stretching vibrations of the O-H and N-H groups. The bands of medium intensities at 3107, 3019 and 2867 cm⁻¹ have been assigned to the C-H stretching modes. The strong band observed at 2729 cm⁻¹ was attributed to $\nu_{sym}(\text{NH}_2^+)$. The band at 1624 cm⁻¹ was assigned to the O-H in-plane deformation. The bands at 1501, 1455 and 1400 cm⁻¹ were assigned to CH₃ and CH₂ deformation modes. The bands of medium intensities at 1369, 1227 and 1193 cm⁻¹ were assigned to C-N stretching. The bands at 1137, 1041 and 983 cm⁻¹ were attributed to asymmetric and symmetric C-C stretching modes. Finally the infrared bands observed in the range 940 - 500 cm⁻¹ were assigned to CCN group deformation vibrations.

3. 4. UV-Visible spectroscopy

The solid state electronic spectrum of the title compound is shown in Fig. 9. Two strong absorptions appear at 275 and 625 nm. The first band is assigned to chloride to copper charge

transfer $\text{Cl} \rightarrow \text{Cu}$ LMCT transition [44]. The second band, in the visible region, corresponds to $\text{Cu} \rightarrow \text{Cl}$ MLTC and intra-ligand CT transition. The transition may be assigned as the $d_{xy}, d_{xz}, d_{yz}, d_{z^2} \rightarrow d_{x^2-y^2}$ [45].

4. Conclusions

We have obtained a new halocuprate salt, $(\text{C}_6\text{H}_{18}\text{N}_3)_4[\text{CuCl}_5]_2[\text{CuCl}_4]_3 \cdot 1.42\text{H}_2\text{O}$ crystals, which crystallize in orthorhombic *Cmca* space group. In the structure, the coordination polyhedra around the three crystallographically independent Cu(II) atoms are different. Cu1, Cu2 and Cu3 have distorted square pyramidal, square planar and distorted tetrahedral environments, respectively. The crystal structure is stabilized via the various types of hydrogen bonding interactions, $\text{N-H}\dots\text{Cl}$, $\text{C-H}\dots\text{Cl}$, $\text{C-H}\dots\text{O}$ and $\text{O-H}\dots\text{Cl}$. The Hirshfeld surface analysis reveals that the driving force in the crystal packing is constituted by the interactions of the chloride atoms with Cu, Hno and Hc species. They constitute a large majority of the Hirshfeld contact surface and they are all three significantly enriched. The vibrational absorption bands were identified by infrared spectroscopy. The UV-vis shows two bands. The first one, in the near UV region, at 275 nm is attributed to the chloride to copper charge transfer transition. The second one, in the visible domain, at 625 nm is assigned to the copper to chlorine intra-ligand charge transfer transition.

5. Highlights

- A new organic-inorganic hybrid material $(\text{C}_6\text{H}_{18}\text{N}_3)_4[\text{CuCl}_5]_2[\text{CuCl}_4]_3 \cdot 1.42\text{H}_2\text{O}$ crystals were synthesized.
- The crystal X-ray structure has been determined.
- Hirshfeld surface analysis was used to evaluate intermolecular contacts.
- Vibrational properties were studied by infrared spectroscopy.
- The UV-Vis spectrum shows two absorption peaks at 275 and 625 nm.

Supplementary material

Crystallographic data for the structural analysis have been deposited at the Cambridge Crystallographic Data Centre, CCDC No 1455800. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK: fax: (+44) 01223-336-033; e-mail: deposit@ccdc.cam.ac.

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Figure Captions

Fig. 1

A view of the asymmetric unit in the crystal structure of the title compound showing the atom-numbering scheme and displacement ellipsoids drawn at the 50% probability level. The dotted lines indicate hydrogen bonds.

Fig. 2

The coordination of Cu in $(\text{C}_6\text{H}_{18}\text{N}_3)_4[\text{CuCl}_5]_2[\text{CuCl}_4]_3 \cdot 1.42(\text{H}_2\text{O})$.

Fig. 3

Projection, along the a -axis, of a layer in the structure of the title compound. The dotted lines indicate hydrogen bonds.

Fig. 4

Projection of the crystal structure of $(\text{C}_6\text{H}_{18}\text{N}_3)_4[\text{CuCl}_5]_2[\text{CuCl}_4]_3 \cdot 1.42(\text{H}_2\text{O})$ in the (a, c) plane, with hydrogen bonds indicated as dashed lines.

Fig. 5

Chains between $\text{Cu}_3\text{Cl}_4^{2-}$ and water molecules in $(\text{C}_6\text{H}_{18}\text{N}_3)_4[\text{CuCl}_5]_2[\text{CuCl}_4]_3 \cdot 1.42(\text{H}_2\text{O})$. The dotted lines indicate hydrogen bonds.

Fig. 6

View of the Hirshfeld surface around the eight independent chloride atoms in the crystal. The surface is colored according to the exterior atom contributing most to the spherical electron density. Cl: Green, Hc: grey, Ho/n: light blue, C: black, N: blue, O: red, Cl: green and Cu: orange. The organic cation and water molecules of the asymmetric are also show.

Fig. 7

Nature of interactions of the eight chloride atoms. The average value and standard deviation of each contact type is shown on the right.

Fig. 8

Infrared spectra of $(\text{C}_6\text{H}_{18}\text{N}_3)_4[\text{CuCl}_5]_2[\text{CuCl}_4]_3 \cdot 1.42(\text{H}_2\text{O})$.

Fig. 9

The UV-Vis spectrum of $(\text{C}_6\text{H}_{18}\text{N}_3)_4[\text{CuCl}_5]_2[\text{CuCl}_4]_3 \cdot 1.42(\text{H}_2\text{O})$.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8

Fig. 9

Table 1 Main interatomic distances (Å) and angles (°) of (C₆H₁₈N₃)₄[CuCl₅]₂[CuCl₄]₃ 1.42(H₂O).

Inorganic anion			
Cu1—Cl6	2.2888 (5)	Cu2—Cl5 ⁱⁱⁱ	2.3008 (5)
Cu1—Cl9 ⁱ	2.3160 (4)	Cu2—Cl5	2.3009 (5)
Cu1—Cl9	2.3160 (4)	Cu3—Cl10 ^{iv}	2.2402 (4)
Cu1—Cl4	2.3421 (5)	Cu3—Cl10	2.2402 (4)
Cu1—Cl7	2.7023 (5)	Cu3—Cl11 ^{iv}	2.2650 (4)
Cu2—Cl8 ⁱⁱ	2.2675 (5)	Cu3—Cl11	2.2650 (4)
Cu2—Cl8	2.2676 (5)		
Cl6—Cu1—Cl9 ⁱ	91.474 (10)	Cl8 ⁱⁱ —Cu2—Cl5 ⁱⁱⁱ	90.0
Cl6—Cu1—Cl9	91.475 (10)	Cl8—Cu2—Cl5 ⁱⁱⁱ	90.0
Cl9 ⁱ —Cu1—Cl9	162.99 (2)	Cl8 ⁱⁱ —Cu2—Cl5	90.0
Cl6—Cu1—Cl4	178.711 (19)	Cl8—Cu2—Cl5	90.0
Cl9 ⁱ —Cu1—Cl4	88.338 (10)	Cl5 ⁱⁱⁱ —Cu2—Cl5	180.0
Cl9—Cu1—Cl4	88.337 (10)	Cl10 ^{iv} —Cu3—Cl10	136.05 (2)
Cl6—Cu1—Cl7	94.989 (18)	Cl10 ^{iv} —Cu3—Cl11 ^{iv}	99.367 (15)
Cl9 ⁱ —Cu1—Cl7	98.213 (10)	Cl10—Cu3—Cl11 ^{iv}	100.144 (15)
Cl9—Cu1—Cl7	98.214 (10)	Cl10 ^{iv} —Cu3—Cl11	100.142 (15)
Cl4—Cu1—Cl7	86.300 (17)	Cl10—Cu3—Cl11	99.366 (15)
Cl8 ⁱⁱ —Cu2—Cl8	180.0	Cl11 ^{iv} —Cu3—Cl11	126.15 (2)

Symmetry codes: (i) $-x, y, z$; (ii) $-x, -y, -z+2$; (iii) $x, -y, -z+2$; (iv) $x, -y+1, -z+1$. **Table 2** Bond length (Å) and angles (°) in the hydrogen bonding scheme of (C₆H₁₈N₃)₄[CuCl₅]₂[CuCl₄]₃ 1.42(H₂O).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
O1—H1E···Cl11 ^{iv}	0.85	2.45	3.1523 (7)	141
N1—H1A···Cl11 ^v	0.91	2.65	3.4783 (14)	152
N1—H1B···Cl5	0.91	2.63	3.3679 (13)	139
N1—H1B···Cl8	0.91	2.63	3.3342 (13)	135
C1—H1C···Cl6 ^{vi}	0.99	2.61	3.5718 (15)	164
C1—H1D···Cl4	0.99	2.89	3.5842 (15)	128
N2—H2···Cl4	1.00	2.49	3.2886 (12)	136
N2—H2···Cl9	1.00	2.36	3.1728 (12)	137
C2—H2A···Cl6 ^{vii}	0.99	2.91	3.8970 (15)	175
C2—H2B···Cl11 ^v	0.99	2.75	3.6070 (15)	145
C4—H4A···Cl10 ^v	0.99	2.74	3.5888 (15)	144
C4—H4B···O1 ^{viii}	0.99	2.33	3.249 (2)	154
C5—H5A···Cl10	0.99	2.72	3.5515 (14)	142
C5—H5B···Cl10 ^v	0.99	2.79	3.5967 (15)	139
C5—H5B···Cl11 ^{ix}	0.99	2.90	3.7672 (14)	147
C6—H6A···Cl6 ^{vii}	0.99	2.70	3.6504 (15)	160
C6—H6B···Cl9 ^{vii}	0.99	2.94	3.4845 (14)	116
C3—H3A···Cl7	0.99	2.93	3.8363 (15)	153
C3—H3B···Cl11 ^x	0.99	2.87	3.6820 (16)	140
N3—H3C···Cl8 ^{vii}	0.91	2.64	3.2309 (12)	123
N3—H3C···Cl10	0.91	2.51	3.3333 (13)	151
N3—H3D···Cl7 ^{vii}	0.91	2.25	3.1548 (13)	176
N3—H3E···Cl4	0.91	2.51	3.2312 (13)	137
N3—H3E···Cl9	0.91	2.58	3.3346 (12)	141

Symmetry codes: (iv) $x, -y+1, -z+1$; (v) $-x+1/2, y, -z+3/2$; (vi) $-x, -y+1/2, z+1/2$; (vii) $x, y+1/2, -z+3/2$; (viii) $x, y-1/2, -z+3/2$; (ix) $-x+1/2, -y+1, z+1/2$; (x) $x, -y+1/2, z+1/2$.

Table 3 Nature of contacts on the Hirshfeld surface around the cation, the three Cu and eight independent Cl⁻ moieties. The second row shows the chemical contents S_x on the surface. N (0.4%) and C (1.6%) species are very rare on the surface and are omitted in the Table. The actual contacts C_{xy} and their enrichment ratios E_{xy} are then shown. The E_{xy} values are obtained from the ratio C_{xy}/R_{xy} , where R_{xy} are the equiprobable contacts. The major contacts ($C_{xy}>20\%$) are in bold. The enrichment values significantly larger than unity are in bold. Underlined enrichment values refer to the major disfavored contacts for which $R_{xy}>4\%$.

	Cl	Ho/n	O	Hc	Cu
% surface	42.6	18.3	2.8	22.7	11.7
Cl	4.9		C_{xy} %	contacts	
Ho/n	24.2	0.3			
O	0.6	0.0	0.0		
Hc	28.0	5.8	3.2	2.6	
Cu	23.2	0.5	0.0	3.1	0.0
Cl	0.27		E_{xy}	Enrichment	
Ho/n	1.56	0.08			
O	0.26	0.00	0.00		
Hc	1.45	<u>0.70</u>	2.47	<u>0.50</u>	
Cu	2.34	<u>0.12</u>	0.00	<u>0.58</u>	0.00