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Synthesis, crystal structure and Hirshfeld surface analysis of the $[Cu_2(3,5\text{-dimethyl-1}H\text{-pyrazole})_4(ClO_4)_2]$ complex

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A new crystalline $[Cu^{I}_2(DIMPA)_4(ClO_4)_2]$ complex has been obtained by the alternating-current electrochemical technique from a water-ethanol solution of 3,5-dimethyl-1*H*-pyrazole (*DIMPA*) and $Cu(ClO_4)_2$, and its crystal has been studied by single-crystal X-ray diffraction. The crystal structure is monoclinic, space group $P2_1/n$, $Z = 4$, $a = 13.834(3)$, $b = 10.170(3)$, $c = 20.610(5)$ Å, $\beta = 96.13(3)°$, $V = 2883.1(13)$ Å^3 (at 100 K). The two independent Cu(I) atoms adopt different coordination environments, formed by two N atoms of two neighboring *DIMPA* molecules and one or two O atoms of a ClO_4^- anion. To analyze the hydrogen bonding pattern in the structure, a Hirshfeld surface analysis was performed.

Copper(I) / σ-Complex / Dimethylpyrazole / Crystal structure / *AC*-electrochemical technique / Hirshfeld surface analysis

1. Introduction

Coordination compounds of pyrazoles have found a wide range of key applications involving their catalytic, magnetic, luminescence, optoelectronic, *etc.* properties [1,2]. The presence of two neighboring nitrogen atoms in the pyrazole ring, both of which are able to coordinate different metal ions, makes pyrazole derivatives efficient “building blocks” for pharmaceutical and agricultural research, and crystal engineering of organometallic frameworks and porous coordination polymers [3]. 3,5-Dimethylpyrazole (*DIMPA*) is among the simplest representatives of such heterocycles. It is characterized by high basicity (due to the inductive effect of the methyl groups) in comparison with simple pyrazole, and has been intensively studied in coordination to different transition metals during several decades. Despite the fact that the coordination behavior of *DIMPA* towards $Cu^{II}(ClO_4)_2$ is represented by 10 entries in Cambridge Crystallographic Database [4-10], unfortunately there is no crystallochemical information about analogous Cu(I) perchlorate compounds. To analyze the coordination abilities of Cu(I) as a “soft acid” towards *DIMPA* (possessing border-line basicity) in the presence of perchlorate anions, we undertook the synthesis and structural characterization of the new complex compound $[Cu_2(DIMPA)_4(ClO_4)_2]$ (**1**).

2. Experimental

3,5-Dimethyl-1*H*-pyrazole (*DIMPA*) was prepared from commercially available acetylacetone and hydrazinium carboxylate, in accordance with the procedure described by Lee *et al.* [11].

2.1. Preparation of complex 1

Crystals of the complex **1** were obtained by alternating-current electrochemical synthesis [12], starting from a water-ethanol solution of *DIMPA* and copper(II) perchlorate. The prepared solution was placed into a small 5 mL test-tube and copper-wire electrodes in cork were inserted. After the application of an alternating-current tension (frequency 50 Hz) of 0.6 V for 17 days good-quality colorless crystals of **1** appeared on the copper electrodes. The yield was about 20%. M.p. 211°C.

2.2. Single-crystal X-ray diffraction studies

Diffraction data for a crystal of **1** were collected on an Oxford Diffraction Xcalibur four-circle diffractometer with Mo K_α radiation ($\lambda = 0.71073$ Å) and an Atlas CCD detector. The diffraction data collected for **1** were processed with the CrysAlis PRO program [13]. The structure was solved using the SHELXT program and refined by the least-squares method on F^2 by SHELXL with graphical user interfaces of

OLEX^2 [14,15]. The atomic displacements for the non-hydrogen atoms were refined using an anisotropic model. All the hydrogen atoms were placed in ideal positions and refined as riding atoms with fixed distances and the following displacement parameters: $U_{iso}(H) = 1.2U_{eq}(C/N)$ and $1.5U_{eq}(C)$ for sp^2 and sp^3 hybridized atoms, respectively. The crystal appeared to be a pseudo-merohedral twin with two components, rotated with respect to each other by ~180° around the direct space **a**-axis and the majority of the reflections overlapped. Data reduction was conducted taking into account both twin domains and produced a HKLF type 5 file with 1234 unique and 21104 overlapping reflections. The final refined twin ratio was 0.9308(3):0.0692(3). The data collection and the refinement parameters are summarized in Table 1. Fractional atomic coordinates and displacement atomic parameters for **1** are listed in Table 2. Hirshfeld surfaces of the molecules in complex **1** and fingerprint plots were produced by CrystalExplorer software [16,17].

3. Results and discussion

The independent part of the structure of **1** is represented by four *DIMPA* molecules, which are pairwise coordinated to two Cu(I) ions. Therefore, the metal centers adopt a practically linear environment, composed of two available N atoms of two ligand moieties, forming $\{Cu(DIMPA)_2\}^+$ cationic fragments (Fig. 1). The coordination environment of the two independent copper(I) ions is completed by weakly coordinated O atoms of ClO_4^- anions (Fig. 2, Table 3). Taking into account that the Cu(1)-O(11) distance is shorter (2.792(3) Å) than the sum of the corresponding Van der Waals radii (2.92 Å), as reported by Bondi [18,19], the Cu(1) arrangement may be considered as T-shaped, including one O and two N atoms. In contrast, the Cu(2)-O(11) distance is longer and equals 2.933(3) Å. The O(21) atom of the second perchlorate anion is 2.974(3) Å away from Cu(2). Both the Cu(2)-O(11) and Cu(2)-O(21) distances are markedly shorter than the the sum of the most recent Van der Waals radii of Cu and O (3.51 Å), reported by Batsanov [20]. Therefore, according to the geometric index proposed by Addison *et al.* [21], the geometrical environment of the Cu(2) metal center can be treated as a seesaw arrangement ($\tau4 = 0.46$) (Fig. 3). The distance from the oxygen atom O(21) to Cu(1) is 3.720(3) Å. As a result, the perchlorate O(11) atom acts as a bridge between Cu(1) and Cu(2), connecting two $\{Cu(DIMPA)_2\}^+$ units into a $\{Cu_2(DIMPA)_4(ClO_4)\}^+$ fragment, which is then completed by one more anion. In the resulting $[Cu_2(DIMPA)_4(ClO_4)_2]$ binuclear complex each linear $\{Cu(DIMPA)_2\}^+$ block is rotated by 180° with respect to the Cu(1)–Cu(2) axis, so that both *DIMPA* molecules are involved in intramolecular N–H…O hydrogen bonding with the same anion. The methyl hydrogen atoms of the ligand form weak C–H…O hydrogen bonds with the second perchlorate anion and the anions from a neighboring $[Cu_2(DIMPA)_4(ClO_4)_2]$ unit (Fig. 4). The average Cu-N distance in **1** is 1.861(3) Å. Within the $[Cu_2(DIMPA)_4(ClO_4)_2]$ unit the Cu(1) and Cu(2) atoms are 3.502(3) Å away from one another.

Table 1 Crystal data and structure refinement for the compound **1** $^{\mathbf{a}}$.

Empirical formula	$C_{20}H_{32}Cl_2Cu_2N_8O_8$	$F(000)$	1456
Formula weight, g mol^{-1}	710.51	Color, shape	colorless, block
Temperature, K	100.0(1)	Theta range for data collection, deg	1.9-29.6
Wavelength, Å	0.71073	Limiting indices	$-19 \le h \le 18$, $-13 \le k \le 13$, $-27 \le l \le 28$
Crystal system, space group	monoclinic, $P2_1/n$	Refinement method	full-matrix least-squares on F^2
Unit cell dimensions:			
a, Å	13.834(3)	Measured reflections	22338
b, Å	10.170(3)	Unique reflections	7824
c, Å	20.610(5)	Reflections $[I > 2\sigma(I)]$	5214
α, °	90	Free parameters	370
β, °	96.13(3)	Goodness-of-fit on F^2	1.07
γ, °	90	R values	$R_1 = 0.043$, $wR_2 = 0.099$
V, Å^3	2883.1(13)	Largest diff. peak and hole, e·Å^{-3}	0.55 and −0.57
Formula units per cell, Z	4		
Absorption coeff., mm^{-1}	1.72	Calculated density, g·cm^{-3}	1.637

[a] CCDC 1476631 contains the supplementary crystallographic data for this paper. Copies of the data can be obtained free of charge on applications to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int.code+(1223)336–033; e-mail for inquiry: fileserv@ccdc.cam.ac.uk).

Table 2 Fractional atomic coordinates and (equivalent) isotropic displacement parameters [a] (Å^2) for **1.**

Atom	*x*	*y*	*z*	$U_{\mathrm{iso}}/U_{\mathrm{eq}}$ [a]
Cu1	0.86381(3)	0.47553(5)	0.48152(2)	0.02273(12)
Cu2	0.62899(3)	0.41510(4)	0.52325(2)	0.02129(12)
Cl1	0.88655(6)	0.19267(9)	0.59641(3)	0.02180(19)
Cl2	0.59329(6)	0.72557(9)	0.38478(4)	0.0223(2)
O11	0.81226(16)	0.2816(2)	0.56730(11)	0.0289(6)
O12	0.96729(17)	0.2696(3)	0.62605(11)	0.0319(6)
O13	0.91969(17)	0.1117(3)	0.54532(10)	0.0296(6)
O14	0.8487(2)	0.1111(3)	0.64425(11)	0.0391(7)
O21	0.6318(2)	0.6584(3)	0.44345(10)	0.0436(8)
O22	0.56283(16)	0.6268(2)	0.33622(10)	0.0257(6)
O23	0.66718(16)	0.8071(3)	0.36224(11)	0.0301(6)
O24	0.51116(18)	0.8045(3)	0.39735(13)	0.0471(8)
N11	0.88689(18)	0.5904(3)	0.55209(11)	0.0181(6)
N12	0.91016(19)	0.5486(3)	0.61392(12)	0.0216(7)
N21	0.84785(18)	0.3639(3)	0.41000(12)	0.0202(6)
N22	0.85718(18)	0.2306(3)	0.41554(12)	0.0192(6)
N31	0.64637(18)	0.5333(3)	0.59266(11)	0.0177(6)
N32	0.64197(18)	0.6663(3)	0.58289(11)	0.0174(6)
N41	0.60841(18)	0.3062(3)	0.44995(11)	0.0166(6)
N42	0.58886(18)	0.3574(3)	0.38894(11)	0.0186(6)
C13	0.9224(2)	0.6484(4)	0.65673(15)	0.0197(8)
C14	0.9056(2)	0.7613(4)	0.62063(15)	0.0199(8)
C15	0.8835(2)	0.7219(4)	0.55550(15)	0.0209(8)
C16	0.8578(2)	0.8029(4)	0.49596(15)	0.0269(8)
C17	0.9445(2)	0.6234(4)	0.72819(14)	0.0242(8)
C23	0.8470(2)	0.1711(4)	0.35686(14)	0.0170(7)
C24	0.8302(2)	0.2688(4)	0.31147(15)	0.0210(8)
C25	0.8308(2)	0.3871(4)	0.34529(14)	0.0185(8)
C26	0.8161(2)	0.5236(4)	0.32019(16)	0.0284(9)
C27	0.8559(3)	0.0259(4)	0.35096(17)	0.0313(9)
C33	0.6586(2)	0.7336(4)	0.63915(14)	0.0182(8)
C34	0.6731(2)	0.6411(3)	0.68749(14)	0.0186(8)
C35	0.6659(2)	0.5185(4)	0.65781(14)	0.0184(8)
C36	0.6797(2)	0.3851(4)	0.68740(15)	0.0261(9)
C37	0.6598(2)	0.8804(4)	0.64058(15)	0.0254(8)
C43	0.5813(2)	0.2630(4)	0.34311(14)	0.0198(8)
C44	0.5975(2)	0.1456(4)	0.37535(14)	0.0199(8)
C45	0.6142(2)	0.1757(3)	0.44167(14)	0.0167(7)
C46	0.6359(2)	0.0837(4)	0.49811(15)	0.0259(8)
C47	0.5610(2)	0.2962(4)	0.27227(14)	0.0256(9)
H12	0.9166	0.4652	0.6250	0.026
H14	0.9084	0.8489	0.6367	0.024
H16A	0.8799	0.7582	0.4581	0.040
H16B	0.8896	0.8889	0.5015	0.040
H16C	0.7872	0.8149	0.4891	0.040
H17A	0.8836	0.6136	0.7480	0.036
H17B	0.9816	0.6975	0.7485	0.036
H17C	0.9829	0.5426	0.7349	0.036
H24	0.8201	0.2578	0.2655	0.025
H26A	0.7488	0.5507	0.3234	0.043
H26B	0.8294	0.5269	0.2745	0.043
H26C	0.8605	0.5832	0.3462	0.043
H27A	0.9166	−0.0034	0.3755	0.047
H27B	0.8562	0.0021	0.3049	0.047
H27C	0.8007	−0.0166	0.3686	0.047
H34	0.6857	0.6578	0.7330	0.022
H36A	0.6422	0.3207	0.6597	0.039
H36B	0.6572	0.3853	0.7309	0.039
H36C	0.7488	0.3617	0.6910	0.039
H37A	0.7178	0.9125	0.6221	0.038
H37B	0.6610	0.9108	0.6858	0.038
H37C	0.6015	0.9142	0.6148	0.038
H44	0.5974	0.0605	0.3563	0.024
H46A	0.7047	0.0588	0.5018	0.039
H46B	0.5956	0.0047	0.4911	0.039
H46C	0.6217	0.1273	0.5384	0.039
H47A	0.5336	0.3851	0.2677	0.038
H47B	0.5143	0.2330	0.2511	0.038
H47C	0.6215	0.2925	0.2517	0.038

[a] For non-hydrogen atoms U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor, for hydrogen atoms U_{iso}.

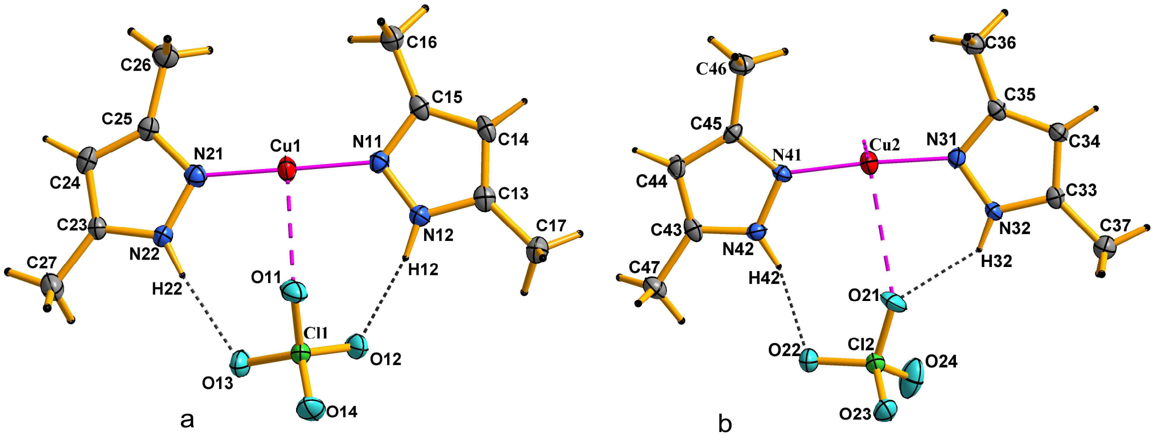

Fig. 1 Independent parts for Cu(1) (a) and Cu(2) (b) in the structure of **1**.

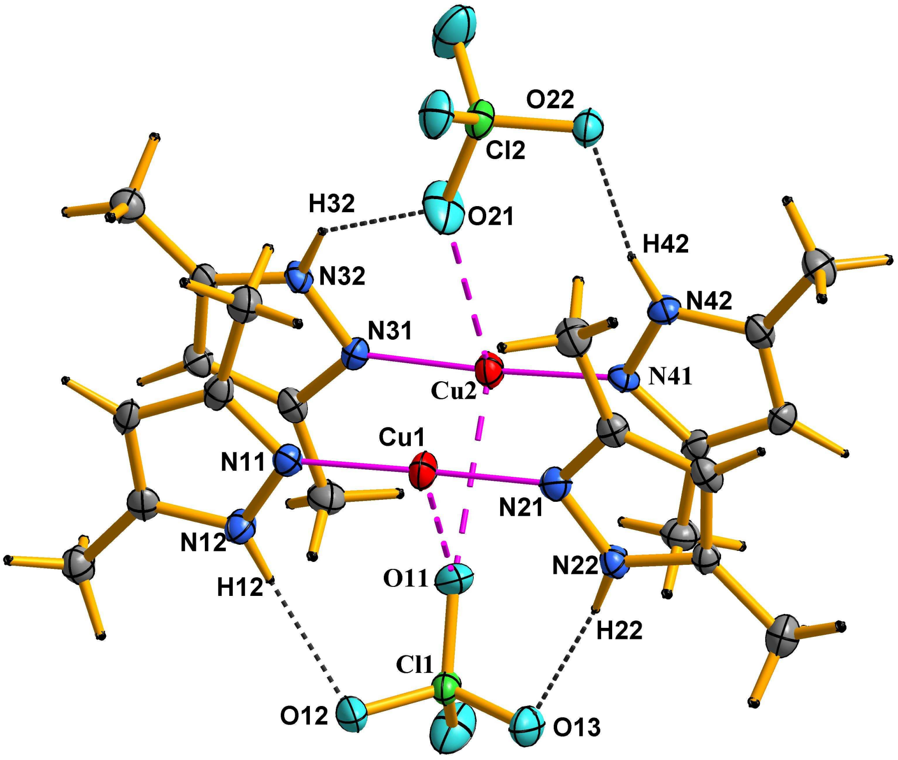

Fig. 2 Dimeric [$Cu_2(DIMPA)_4(ClO_4)_2$] moiety in **1**.

Table 3 Selected bond lengths (Å) and angles (°) in the structure of **1**.

Bond	Value	Angle	Value
Cu1–N21	1.855(3)	N21–Cu1–N11	176.70(11)
Cu1–N11	1.866(3)	N31–Cu2–N41	176.06(12)
Cu2–N31	1.864(3)	O11–Cu1–N11	89.01(10)
Cu2–N41	1.870(3)	O11–Cu1–N21	93.10(11)
Cu1–O11	2.792(3)	O11–Cu2–N31	91.41(10)
Cu2–O11	2.933(3)	O11–Cu2–N41	91.60(10)
Cu2–O21	2.974(3)	N11–Cu1–N21	176.70(12)
Cu1–Cu1	3.502(3)	N31–Cu2–N41	176.05(13)
Cu1–O21	3.720(3)	Cu1–O11–Cu2	75.40(10)
		O11–Cu2–O21	119.63(11)

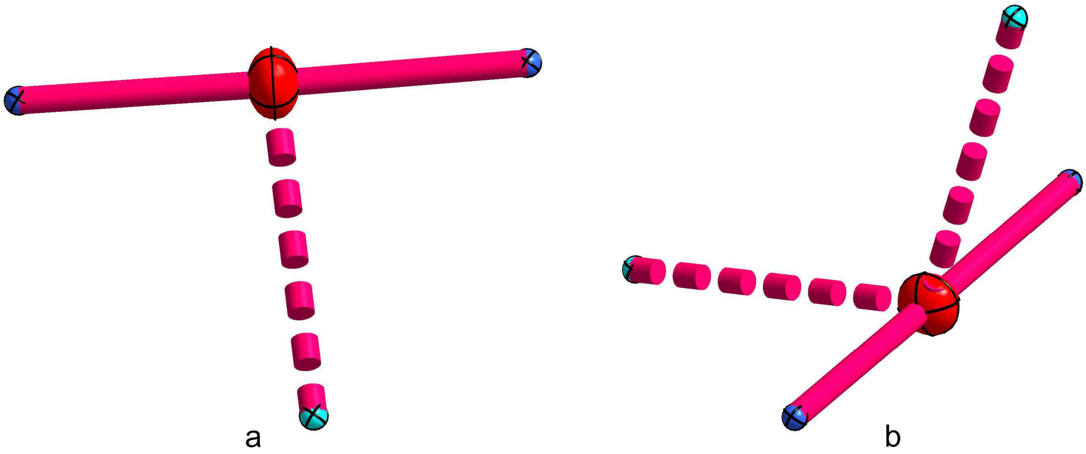

Fig. 3 Different types of Cu(I) arrangement in the complex **1**: T-shaped for Cu(1) (a), seesaw for Cu(2) (b).

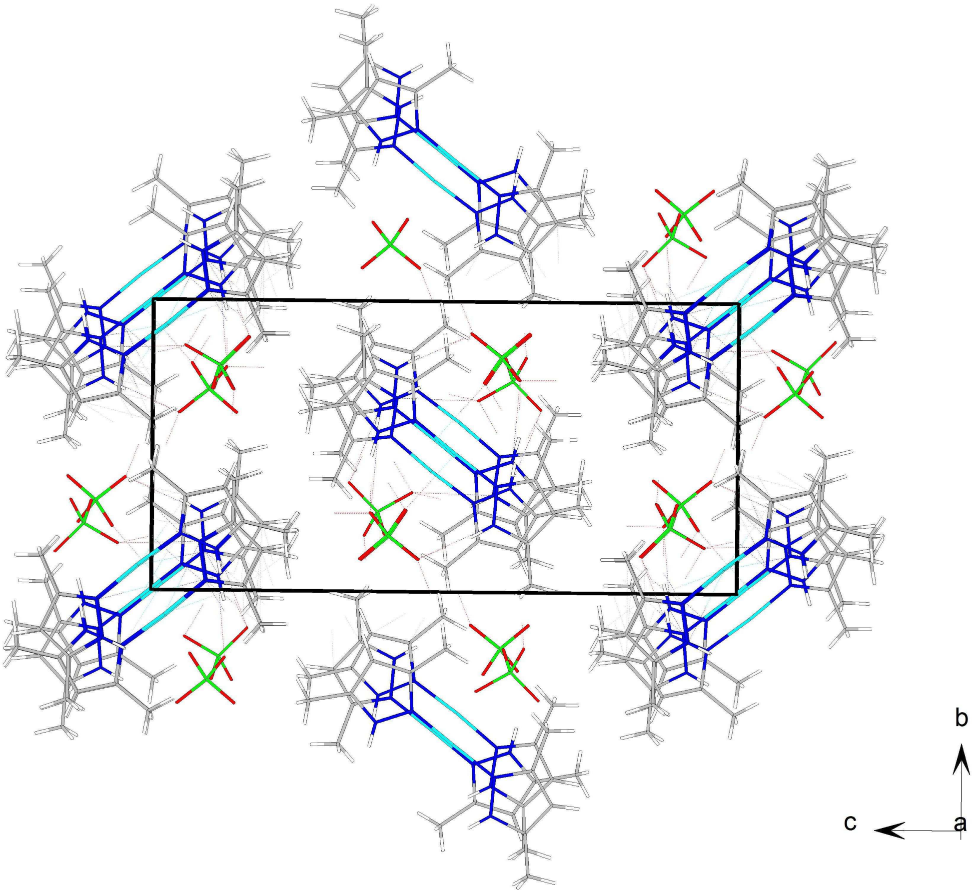

Fig. 4 Crystal packing of **1** viewed along [-100].

4. Hirshfeld surface analysis

Hirshfeld surfaces (with d_{norm} mapped) and fingerprints (d_e *versus* d_i) were generated for the $\{Cu(DIMPA)_2\}^+$ cations in the reported structure, using Crystal Explorer [16,17]. Analysis of the Hirshfeld surfaces (Fig. 5) reveals several common features of the $\{Cu(DIMPA)_2\}^+$ cations and highlights their role in the crystal-packing organization. The cations are characterized by the presence of two strong N–H…O hydrogen bonds with perchlorate anions (Table 4). The structural units are also involved in C–H…O bonding, which is reflected on the surfaces as weak red and white areas. Fingerprint plots were produced to show the intermolecular surface bond distances; the regions of (N)H….O(Cl) and Cu….O bonding are highlighted. The contribution of π…π-stacking between pyrazole rings of the same $[Cu_2(DIMPA)_4(ClO_4)_2]$ dimer to the surface area is about 10%.

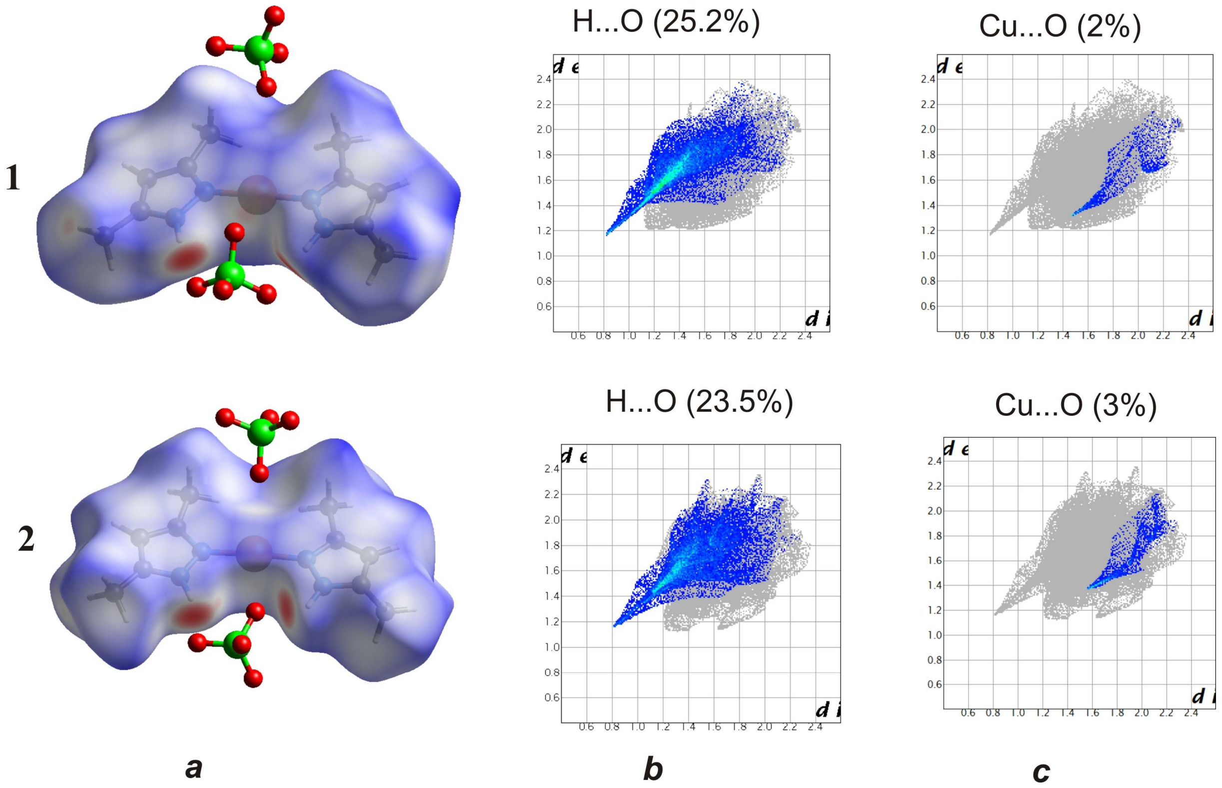

Fig. 5 Hirshfeld surface analysis of the $\{Cu(DIMPA)_2\}^+$ cations in **1**. (***a***) Hirshfeld surfaces mapped with d_{norm}, highlighting both donor and acceptor ability. (***b***) Fingerprint plots for $\{Cu(DIMPA)_2\}^+$ units resolved into O…H bonds. (***c***) Fingerprint plots for $\{Cu(DIMPA)_2\}^+$ units resolved into Cu…O bonds. The full fingerprint appears in gray beneath each decomposed plot.

Table 4 Geometry of main hydrogen bonds in the structure of **1**.

Atoms involved D−H···A	Symmetry	Distances, Å			Angle, °
		D···H	H···A	D···A	D−H···A
N(12)−H(12)···O(12)		0.88	2.11	2.949(4)	159
N(22)−H(22)···O(13)		0.88	2.11	2.978(4)	169
N(32)−H(32)···O(21)		0.88	2.13	2.863(3)	140
N(42)−H(42)···O(22)		0.88	2.09	2.955(4)	166
C(16)−H(16B)···O(13)	*x*, *y*+1, *z*	0.98	2.46	3.383(5)	157
C(27)−H(27C)···O(23)	*x*, *y*–1, *z*	0.98	2.57	3.457(5)	151
C(46)−H(46C)···O(24)	–*x*+1, –*y*+1, –*z*+1	0.98	2.48	3.318(4)	144

References

[1] L. Yet, in: *Reference Module in Chemistry, Molecular Sciences and Chemical Engineering, Comprehensive Heterocyclic Chemistry III*, Vol. 4, 2008, pp. 1-141.

[2] F.K. Keter, J. Darkwa, *Biometals* 25 (2012) 9-21.

[3] C. Pettinari, A.Tăbăcaru, S. Galli, *Coord. Chem. Rev*. 307 (2016**)** 1-31.

[4] F.H. Allen, *Acta Crystallogr. B* 58 (2002) 380-388.

[5] I. Banerjee, M. Dolai, A.D. Jana, K.K. Das, M. Ali, *CrystEngComm* 14 (2012) 4972-4975.

[6] I. Castro, M.L. Calatayud, W.P. Barros, J. Carranza, M. Julve, F. Lloret, N. Marino, G. De Munno, *Inorg. Chem.* 53 (2014) 5759-5771.

[7] F. Yu, *Acta Crystallogr. C* 67 (2011) m331-m334.

[8] M.R. Malachowski, A.S. Kasto, M.E. Adams, A.L. Rheingold, L.N. Zakharov, L.D. Margerum, M. Greaney, *Polyhedron* 28 (2009) 393-397.

[9] G.A. van Albada, M.G. van der Horst, I. Mutikainen, U. Turpeinen, J. Reedijk, *Inorg. Chim. Acta* 361 (2008) 3380-3387.

[10] A.R. Oki, J. Sanchez, R.J. Morgan, T.J. Emge, *J. Coord. Chem*. 36 (1995) 167-174.

[11] B. Lee, Ph. Kang, K.H. Lee, J. Cho, W. Nam, W.K. Lee, N.Hw. Hur, *Tetrahedron Lett.* 54 (2013) 1384-1388.

[12] B.M. Mykhalichko, M.G. Mys’kiv. Ukraine Patent UA 25450A, Bull. No. 6, 1998.

[13] *CrysAlis PRO*, Agilent Technologies, Yarnton, UK, 2011.

[14] G.M. Sheldrick, *Acta Crystallogr. C* 71 (2015) 3-8.

[15] O.V. Dolomanov, L.J. Bourhis, R.J. Gildea, J.A.K. Howard, H. Puschmann, *J. Appl. Crystallogr.* 42 (2009) 339-341.

[16] S.K. Wolff, D.J. Grimwood, J.J. McKinnon, M.J. Turner, D. Jayatilaka, M.A. Spackman, *Crystal Explorer*, University of Western Australia, 2012.

[17] M.A. Spackman, D. Jayatilaka, *CrystEngComm* 11 (2009) 19-32.

[18] A. Bondi, *J. Phys. Chem.* 68 (1964) 441-664.

[19] S. Alvarez, *Dalton Trans.* 42 (2013) 8617-8636.

[20] S.S. Batsanov, *Inorg. Mater.* 37 (2001) 871-885.

[21] A.W. Addison, T.N. Rao, J. Reedijk, J. van Rijn, G.C. Verschoor, *J. Chem. Soc.*, *Dalton Trans.* (1984) 1349-1356.