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HIRSHFELD SURFACE ANALYSIS OF A MONONUCLEAR PYRAZOLE-CONTAINING COPPER(II) COMPLEX OBTAINED BY OXIDATIVE DISSOLUTION METHOD

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Abstract

In this work, a method of oxidative dissolution was used to obtain mononuclear copper(II) complex $Cu(C_6H_8N_3O)_2$ with 1-carboxamide-3,5-dimethylpyrazole. The variety of techniques were used to identify and characterize the structure of the complex and the ligand, such as IR and NMR spectroscopy, microanalyses, single-crystal X-ray diffraction. Hirshfeld surface analysis was performed to visualize the close intermolecular atomic contacts in the crystal structure of the title compound. It was found that $Cu(C_6H_8N_3O)_2$ was formed as a result of a multistage process of oxidative dissolution of metallic copper with the participation of air oxygen and ammonium ions. This process leads to the appearance of a sufficient amount of Cu^{2+} ions in the solution, which partially ensures the production of the final compound, as well as the dissolution of zero-valent copper through the formation of intermediate Cu^{1+} compounds, which are oxidized by air oxygen to form divalent copper compounds. It has also been found that ammonium cyanate is formed in parallel through exchange reactions, which undergo dissociation in acetonitrile solutions, and the resulting HNCO undergoes hydrolysis. The hydrolysis products react with the starting ligand 3,5-dimethyl-1H-pyrazole to form 1-carboxamide-3,5-dimethylpyrazole. This acid then reacts with Cu^{2+} ions to form the final mononuclear complex. Single-crystal X-ray diffraction analysis reveals that the title compound crystallizes in the triclinic crystal system, space group $P\bar{1}$ (Z = 2). For the title compound, the most significant contributions to the overall crystal packing are from H···H (47 %), H···O/O···H (19.5 %), H···C/C···H (12.1 %) and H···N/N···H (11.5 %) contacts. According to the Hirshfeld surface analysis, hydrogen bonds (H···H and H···O/O···H) and other close contacts involving hydrogen atoms make the main contribution to intermolecular interactions in the title compound. Two intermolecular NH···O contacts with a length of 2.192 Å are the shortest.

Keywords: pyrazole ligands; copper complexes; crystal structure; oxidative dissolution; Hirshfeld surface analysis.

АНАЛІЗ ПОВЕРХНІ ХІРШФЕЛЬДА МОНОЯДЕРНОГО ПІРАЗОЛВМІСНОГО КОМПЛЕКСУ КУПРУМУ(ІІ), ОТРИМАНОГО МЕТОДОМ ОКИСНОГО РОЗЧИНЕННЯ

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Анотація

У роботі методом окисного розчинення одержано моноядерний комплекс $Cu(C_6H_8N_3O)_2$ з 1-карбоксамід-3,5-диметилпіразолом та запропоновано механізм його утворення. В результаті проведених досліджень у системі металічна мідь – натрій ціанат – амоній хлорид – 3,5-диметил-1Н-піразол – ацетонітрил, встановлено, що окиснення Cu^0 до Cu^{2+} проходить через стадію утворення сполук Cu^{1+}. Окисником по відношенню до купруму може виступати не лише кисень повітря, а й солі Cu(II), які здатні ефективно впливати на її розчинення, взаємодію з вихідними реагентами та формування моно- чи поліядерних комплексів. Далі сполуки Cu^{1+} швидко окиснюються киснем повітря до Cu^{2+} з утворенням кінцевих продуктів, в даному випадку до моноядерного комплексу $Cu(C_6H_8N_3O)_2$. Отриманий комплекс та ліганд проаналізовано за допомогою елементного аналізу, ІЧ та ЯМР-спектроскопії. Методом рентгеноструктурного аналізу встановлено будову отриманої сполуки $Cu(C_6H_8N_3O)_2$. Комплекс складається з майже планарних молекул, а аніон ліганду 1-карбоксамід-3,5-диметилпіразол, що сформований в процесі синтезу, хелатується до атома Cu(II) двома атомами нітрогену: піридиновим та карбоксамідним. Чотири атоми нітрогену від двох аніонів ліганду координуються навколо атома купруму, утворюючи плоскоквадратну структуру CuN_4. До того ж вони розташовані у транс-положенні один до одного. Атоми оксигену O(1) і O(2) від NCO-груп не беруть участі в координації до центрального атома Cu(II). Для дослідження міжмолекулярних взаємодій у кристалічній структурі комплексу було проведено аналіз поверхні Хіршфельда, доповнений двовимірними графіками відбитків. Для зазначеної сполуки найбільший внесок у загальну кристалічну упаковку роблять H···H (47 %), H···O/O···H (19.5 %), H···C/C···H (12.1 %) і H···N/N···H (11.5 %) контакти. Водневі зв'язки (H···H та H···O/O···H) та інші близькі контакти за участю атомів гідрогену роблять основний внесок у міжмолекулярні взаємодії в зазначеній сполуці. Найкоротшими є два міжмолекулярні контакти NH···O з довжиною 2.192 Å.

Ключові слова: піразольні ліганди, комплекси купруму, кристалічна структура, окисне розчинення, аналіз поверхні Хіршфельда.

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Introduction

Pyrazole-based compounds possess diverse biological activities such as analgesic, anticonvulsant, antitumor, antidiabetic, antimicrobial, antipyretic, antiviral, antimalarial, local anesthetic and so forth [1–8]. A spectrum of pharmacological activities has been attributed to pyrazole analogs [9]. The substitution, replacement, or removal of functional groups on a pyrazole ring is consistent with diverse molecular interactions, efficacy, and potency of these analogs [10–12]. Numerous interactions of these derivatives with targets may influence future research and prospects, offering opportunities to optimize therapeutic activity with fewer side effects [13–15]. The investigation of cytotoxic, cytoprotective, anti-inflammatory and antidepressant activities of some pyrazole analogs to study their pharmacological properties and rational design of new analogs is important [16–20]. Pyrazole-based compounds are often used as scaffolds in drug discovery and development due to their versatility. In addition to medicinal applications, pyrazoles serve as important ligands in coordination chemistry. They are involved in the synthesis of metal complexes, which can be used as catalysts in various chemical reactions [21]. Pyrazoles have applications in the agricultural industry as herbicides, fungicides, and insecticides [22]. Their ability to chelate metals makes them useful in the design of chemosensors for detecting metal ions. Pyrazole derivatives are employed in the development of dyes and pigments due to their vivid colors and stability. The electronic properties of pyrazoles make them suitable for use in organic electronics, such as organic light-emitting diodes (OLEDs) [23]. They play a significant role in the development of materials for energy storage, including batteries and supercapacitors. Pyrazoles are also used as building blocks in organic synthesis, facilitating the construction of more complex molecules [24]. The hydrogen bonding capability of pyrazoles contributes to their ability to form supramolecular structures [25]. Pyrazoles can be easily modified by substituting different functional groups, which allows for the creation of various molecular architectures with predictable properties [26]. Drug design necessitates understanding the interactions between active molecules and receptors, exploring the mechanisms of chemical reactions and molecular dynamics, and examining the interactions between molecules in a crystal to comprehend their stability and properties. Hirshfeld surface analysis aids in addressing these challenges. It is also employed to study and visualize the molecular environment in crystals. This technique enables the identification and interpretation of interactions between molecules in the crystal structure, such as hydrogen bonds, Van der Waals forces, and other intermolecular interactions. Based on electron density calculations, this method facilitates the creation of three-dimensional surfaces that represent the spatial distribution of these interactions. Hirshfeld surface analysis allows for quantitative measurements of molecular surface area and molecular volume. It also enables the calculation of globularity and asphericity values to determine the nature of the molecular surface and the anisotropy of the studied molecules [27].

The peculiarity of this work is the use of a unique approach to obtain the title compound, namely, an oxidative dissolution method, in which metal powder is employed as a starting material. Often, unexpected and unpredictable complex formation processes take place under conditions of oxidative dissolution synthesis [40]. It was the authors of this article who first developed and applied this method for the synthesis of many mononuclear and polynuclear complexes based on pyrazole ligands and proved the effectiveness of using copper (II) salts as potential oxidizing agents in the dissolution of zero-valent metals [40]. Undoubtedly, the unique method of oxidative dissolution allowed us to obtain the mononuclear complex characterized in this work, the structure of which was established earlier [29]. In the other works [32-35], the authors started with another reagent and used different synthetic approaches. It should be noted that the complex obtained in this work is polymorphic to the compound described by Valach et al. [34].

Experimental and methods

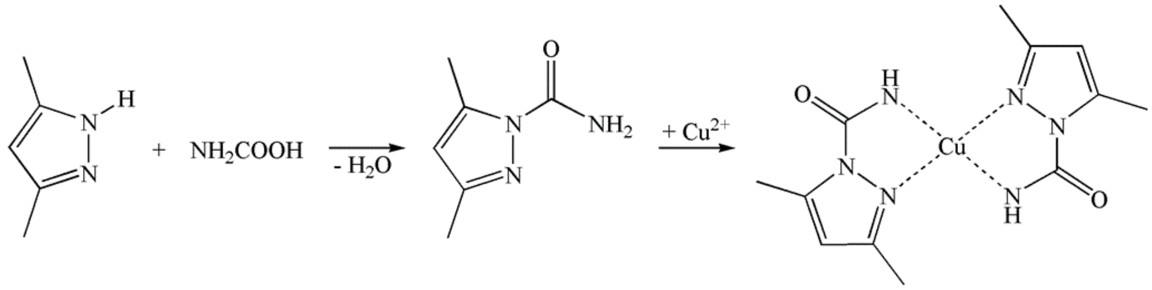
All chemicals and solvents were commercial products of reagent grade and used without further purification. Microanalyses were performed with a Perkin-Elmer 2400 CHN. IR spectra (KBr pellets) were recorded with a Perkin–Elmer Spectrum BX FT-IR in the range of 400–4000 cm^{-1}. ^{1}H NMR spectra were recorded on a Bruker AC-400 spectrometer (400 MHz) at room temperature. X-ray data were collected on a Bruker AXS CCD Smart 1000 diffractometer (monochromated Mo-Kα radiation, $\lambda = 0.71073$ Å) by use of scans at room temperature. The structures were solved with SHELXT and refined on F^2 using all reflections with SHELXL [28]. The structure of the title compound was deposited at the Cambridge Crystallographic Data Centre (№2417706). Hirshfeld surface (HS) analysis: Type – Hirshfeld; Resolution – High (Standard); Isovalue – 0.5; d_{norm} – 0.316 (min), 0.393 (mean), 1.154 (max); Volume 327.50 Å^3, Area 315.07 Å^2, Globularity 0.729, Asphericity 0.209. Fingerprint Breakdown: Filtering fingerprint by element type. The surface area included (as a percentage of the total surface area) for close contacts between atoms inside and outside the surface.

Complex $Cu(C_6H_8N_3O)_2$ was synthesized using the oxidative dissolution method under free access of air oxygen. A mixture of 3,5-dimethyl-1H-pyrazole (0.96 g; 0.01 mol), ammonium chloride (0.535 g; 0.01 mol), and sodium cyanate (0.65 g; 0.01 mol) in 20 mL of acetonitrile (CH_3CN) solution was magnetically stirred with copper powder (0.64 g; 0.01 mol) at room temperature until the solid was completely dissolved. The resulting green solution was filtered, and the filtrate was left to stand at room temperature in the air. The violet needle-shaped crystals of the compound, suitable for X-ray analysis, were formed within 3 days. Yield 65%. IR (KBr (cm^{-1})): 3465, 3350, 3294, 3094, 3019, 2967, 2923, 2857, 1571, 1472, 1410, 1288, 1178, 1149, 1044, 985, 889, 845, 799, 669, 654, 584, 562, 460 and 435. Elemental analysis (%):C, 29.44; H, 2.47; N, 20.68. Found: C, 29.57; H, 2.46; N, 20.70.

The synthesis of 3,5-dimethyl-1H-pyrazole was carried out according to the following method. 24 mL (90 %, 25.03 g, 0.5 mol) of hydrazine hydrate was slowly added dropwise over 30 minutes to 51.2 mL (50 g; 0.5 mol) of acetylacetone, which had been previously cooled to 10°C. The reaction was conducted with continuous stirring and cooling. After a white precipitate formed, stirring was ceased and the solution containing the precipitate was left overnight. The resultant precipitate was filtered using a glass filter, washed with cold ethanol, and dried in air. The yield of the crystalline product, in Scheme 1, was 80 %. IR (KBr (cm^{-1})): 3202, 3132, 3110, 3039, 2992, 2945, 2879, 2788, 2607, 1666, 1595, 1484, 1422, 1306, 1154, 1028, 855, 779, 736, 661, and 403. ^{1}H NMR (DMSO-d_6), δ: 2.14 (s., 6H; $2CH_3$), 5.64 (s., 1H; pz-CH), 11.87 (br. s., 1H; NH). Elemental analysis: calculated (%): C 62.47; H 8.38; N 29.14. Found: C 62.49; H 8.33; N 29.16.

Results and discussion

The formation of the title compound follows scheme 1 [29].



Scheme 1. Synthesis of the title compound

In our work, we utilized a special synthetic approach to prepare $Cu(C_6H_8N_3O)_2$, namely, the oxidative dissolution (OD), in which metal powders are employed as starting materials. It is an effective method for the production of both known and novel homo- and heterometallic polynuclear coordination compounds [30]. Often, the oxidative dissolution of metals leads to unexpected complex formation [31]. Thus, we have found that oxidation Cu^0 to Cu^{2+} passes through the stage of formation of Cu^I compounds. Not only air oxygen but also Cu^{II} salts can serve as oxidants for copper Cu^0, which can influence the efficiency of Cu^0 dissolution and its reaction with the initial (2a, b, c). Under these conditions, ammonium isocyanate is formed through exchange reactions and dissociates in acetonitrile (3a). The resulting HNCO is hydrolysed (3b) and the hydrolysis products react with 3,5-dimethyl-1H-pyrazole to form 1-carboxamide-3,5-dimethylpyrazole. Then 1-carboxamide-3,5-dimethylpyrazole reacts with Cu^{2+} ions to form the final product (Scheme 1).

$$Cu^0 + DMPZ + NH_4Cl + NaNCO + CH_3CN + O_2 \rightarrow Cu(C_6H_8N_3O)_2 + NH_3 + H_2O + NaCl \quad (1)$$

$$Cu^0 + 2NH_4^+ + 0{,}5O_2 \rightarrow [Cu(NH_3)_2]^{2+} + H_2O \quad (2a)$$

$$Cu^0 + Cu^{2+} \rightarrow 2Cu^{1+} \quad (2b)$$

$$2Cu^{1+} + O_2 \rightarrow Cu^{2+} + O_2^{2-}\ (O^{2-}) \quad (2c)$$

$$NH_4NCO \leftrightarrow NH_3 + HNCO \quad (3a)$$

$$HNCO + H_2O \rightarrow NH_2COOH \quad (3b)$$

The resulting mononuclear complex (Fig. 1) consists of almost planar molecules. Single-crystal X-ray diffraction analysis reveals that the title compound crystallizes in the triclinic crystal system, space group $P\overline{1}$ (Z = 2). The Cu^{II} ion displays a slightly distorted square-planar coordination environment (seesaw geometry, τ_4'= 0.234) [36] formed by two pyridine-like nitrogen atoms and two carbamate-like nitrogen atoms of two 1-carboxamide-3,5-dimethylpyrazole ligands coordinated in a bidentate chelating mode. In this case, they are located in a transposition to each other. The oxygen atoms O(1) and O(2) of the NCO groups do not participate in the binding of Cu(II) atoms. The distances Cu - N (carboxamide) are equal to 1.923(9) and 1.931(10) Å and are much shorter than those of Cu - N (pyrazole) (1.998(7) and 2.002(5) Å). The chelate angles are reduced to 81.31(9)° (Table 1).

Table 1

Selected bond lengths (Å) and bond angles (°) for the title compound

Cu1—N2	1.923(9)	N2—Cu1—N1	165.12(8)
Cu1—N1	1.931(10)	N2—Cu1—N4	81.31(9)
Cu1—N4	1.998(7)	N1—Cu1—N4	102.06(8)
Cu1—N3	2.002(5)	N2—Cu1—N3	100.29(9)
		N1—Cu1—N3	81.93(9)
		N4—Cu1—N3	158.57(8)

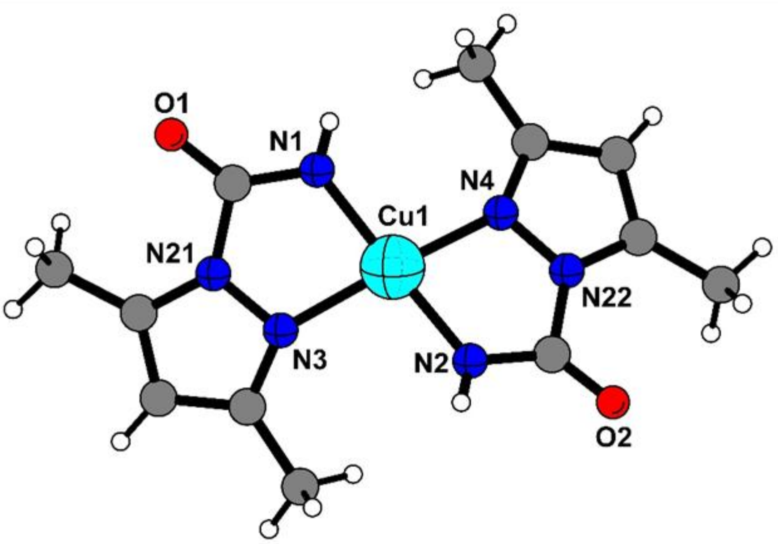


Fig. 1. The molecular structure of the title compound

Hence, the title coordination compound was obtained and described. It is known from the literature an isostructural complex with the same composition was synthesized by a different method using other starting reagents [34–35]. It is worth noting, that the title compound and [34] are not the same, but are two separate polymorphs (Table 2).

Table 2

Comparative crystallographic data, details of data collection, and characteristics of data refinement of the title compound with polymorphic complex [34] and compound [35]

Complexes	The title compound	The compound with CCDC identifier CXAPCU10 [34]	The compound with CCDC identifier CXAPCU11 [35]
Empirical formula	$C_{12}H_{16}Cu_1N_6O_2$	$C_{12}H_{16}Cu_1N_6O_2$	$C_{12}H_{16}Cu_1N_6O_2$
Formula weight	339.86	-	339.85
Temperature, K	293	295	293
Wavelength, Å	0.71073		
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	$P\overline{1}$	$P2_1/c$	$P\overline{1}$
Unit cell dimensions			
a, Å	8,3508(9)	13.697 (7)	8.461 (1)
b, Å	8.6604(8)	14.759 (7)	8.631 (1)
c, Å	10.6739(13)	7.463 (7)	10.745 (2)
α, deg	68.432(9)	-	68.72 (1)
β, deg	69.259(10)	114.01 (3)	70.29 (1)

Continuation of Table 2

γ, deg	77.487(8)	-	77.64 (1)
Volume, Å^3	668.05(12)	1378.14	684.57 (17)
Z	2	4	2
Density (Mg/m^3)	1.690	-	-
μ, mm^{-1}	1.650	-	1.61
F (000)	350	-	-
θ range, deg	2.84 to 28.43	-	-
Reflections collected	5619	-	7666
GOOF	1.087	-	-
$\Delta\rho_{max}$, $\Delta\rho_{min}$, *e* Å^{-3}	0.72–0.55	-	0.65, -0.98

The Hirshfeld surface analysis and the associated two-dimensional fingerprint plots were performed using Crystal Explorer 17.5 software [37], with a standard resolution of the three-dimensional d_{norm} surfaces plotted over a fixed color scale of –0.3156 (red) to 1.1537 (blue) a.u. There are 10 red spots on the d_{norm} surface (Fig. 2).

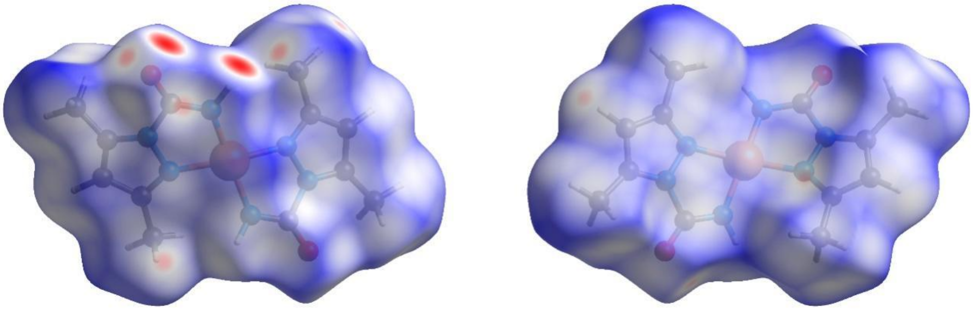


Fig. 2. Two projections of Hirshfeld surfaces mapped over d_{norm} showing the intermolecular interactions within the molecule

The dark-red spots arise as a result of short interatomic contacts and represent negative d_{norm} values on the surface, while the other weaker intermolecular interactions appear as light-red spots. Two intermolecular NH···O contacts with a length of 2.192 Å marked by bright, saturated red spots on the surface, are the shortest (Fig. 3).

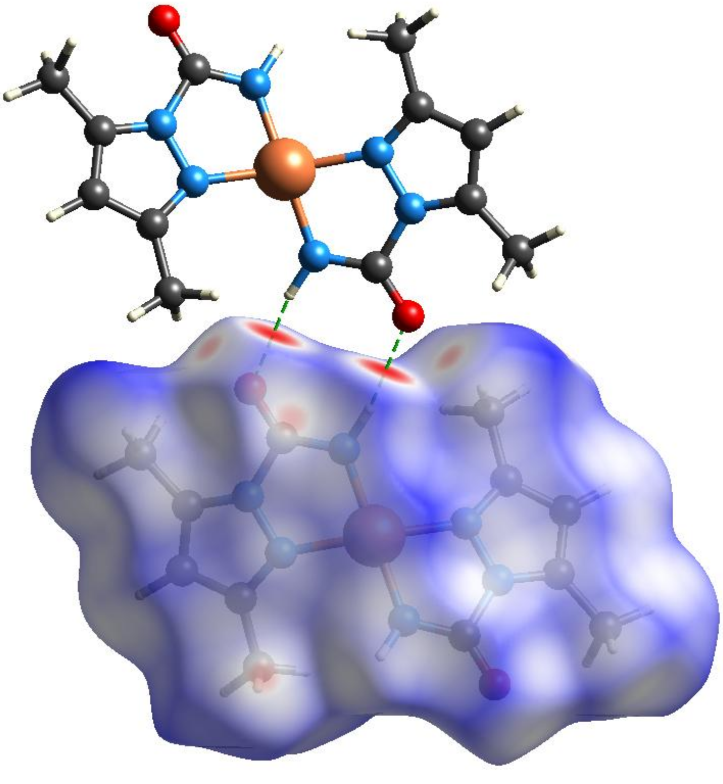


Fig. 3. Visualization of the shortest NH···O intermolecular interactions: the distance between the selected oxygen and hydrogen atoms is represented as a green dashed line. The locations of these short contacts are visualized as bright, saturated red spots on the Hirshfeld surface with the function d_{norm}

The Hirshfeld surfaces mapped over d_{norm} are shown for the H···H (47 %), H···O/O···H (19.5 %), H···C/C···H (12.1 %) and H···N/N···H (11.5 %) contacts, the overall two-dimensional fingerprint plot and the decomposed two-dimensional fingerprint plots are given in Fig. 4.

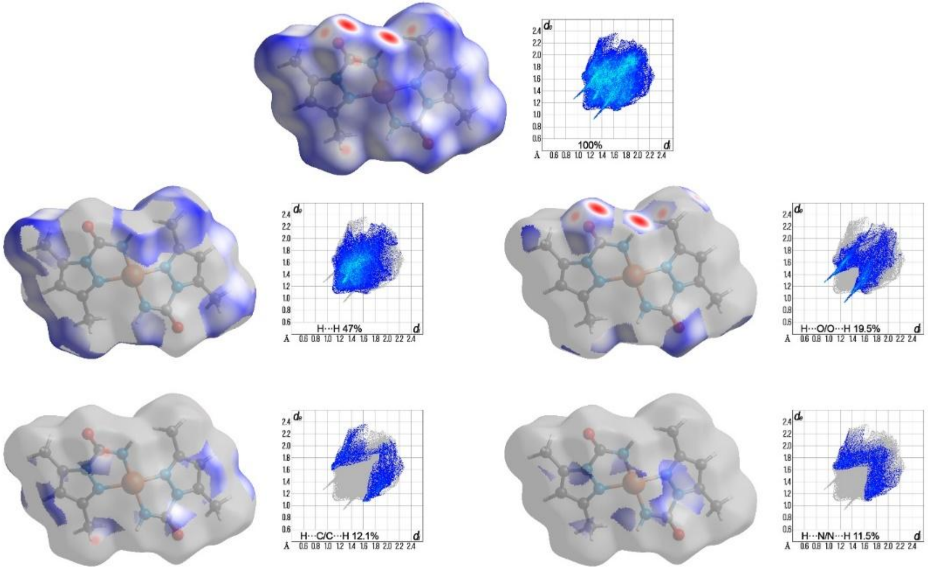


Fig.4. The overall two-dimensional fingerprint plot and those delineated into specified interactions. Hirshfeld surface representations with the function d_{norm} plotted onto the surface for the different interactions

The small contribution of the other weak intermolecular N···C/C···N (3.1 %), Cu···C/C···Cu (2.5 %), N···N (1.5%), Cu···H/H···Cu (1.2 %), C···C (0.9 %) and Cu···N/N···Cu (0.7 %) contacts has a negligible effect on the packing. The relative percentage contributions to the overall Hirshfeld surface by elements (close contacts between the selected atom within the surface and all atoms outside the surface): H···all atoms (66.9 %), O···all atoms (10.9 %), C···all atoms (10.6 %), N···all atoms (9.3 %) and Cu···all atoms (2.4 %). The obtained results were compared with those from a Hirshfeld surface analysis of a polymorphic modification of the title compound [33], which has the same chemical composition but a different crystal packing. The results are very similar. In both cases, the intermolecular contacts involving hydrogen atoms (H···H – 51 %), H···O/O···H – 16.4 %, H···C/C···H – 10.5%, and H···N/N···H – 7.1 % for the polymorph) are the most dominant. It should be noted, that there is a slight increase in the contribution of the intermolecular H···H contacts to the crystal packing, accompanied by a simultaneous decrease in the contributions from the intermolecular H···O/O···H, H···N/N···H, and H···C/C···H contacts. At the same time, the O···N/N···O and O···C/C···O contacts became active. But their contributions to the crystal packing are very small, at 2.4 % and 0.9 %, respectively. The intermolecular Cu···Cu, Cu···O, and O···O contacts are not observed in both cases. Also, quantitative physical properties of the Hirshfeld surface for the title compound were obtained, such as molecular volume (327.5 Å^3), surface area (315.07 Å^2), globularity (0.729), as well as asphericity (0.209). These values were also compared with those of the polymorph. The similarity in molecular volume (338.38 Å^3 for the polymorph), surface area (313.00 Å^2), globularity (0.750), and asphericity (0.227) indicates that the size and shape of these two molecules are also similar. The relative percentage contributions (by elements) and the contribution of individual interactions to the overall Hirshfeld surface were compared with the corresponding data obtained from the Hirshfeld surface analysis for the same complex synthesized and studied by Szécsényi, K.M. *et al.* [35] (Tab. 3, 4). The results of the Hirshfeld surface analysis differed by no more than 0.5 %.

Table 3

Relative percentage contributions of elements to the overall Hirshfeld surface for selected complexes

Interaction	The title compound	The compound with CCDC identifier CXAPCU10 [34]	The compound with CCDC identifier CXAPCU11 [35]
Cu···all atoms	2.4	2.4	2.3
O···all atoms	10.9	10.2	10.8
H···all atoms	66.9	67.6	67.4
N···all atoms	9.3	9.9	9.3
C···all atoms	10.6	10.0	10.2

Table 4

The contributions of individual interactions to the overall Hirshfeld surface for selected complexes

Interaction or quantitative physical properties of the HS	The title compound	The compound with CCDC identifier CXAPCU10	The compound with CCDC identifier CXAPCU11
Cu⋯Cu	0	0	0
Cu⋯N/N⋯Cu	0.7	2.3	0.7
Cu⋯C/C⋯Cu	2.5	0.8	2.3
Cu⋯O/O⋯Cu	0	0	0
Cu⋯H/H⋯Cu	1.2	1.6	1.2
N⋯N	1.5	2.2	1.5
N⋯C/C⋯N	3.1	3.3	3.1
N⋯O/O⋯N	0	2.4	0
N⋯H/H⋯N	11.5	7.1	11.3
C⋯C	0.9	1.5	0.8
C⋯O/O⋯C	0	0.9	0
C⋯H/H⋯C	12.1	10.5	11.7
O⋯O	0	0	0
O⋯H/H⋯O	19.5	16.4	19.3
H⋯H	47.0	51.0	47.9
Globularity	0.729	0.750	0.735
Asphericity	0.209	0.227	0.202
Molecular volume	327.50 Å^3	338.38 Å^3	335.77 Å^3
Surface area	315.07 Å^2	313.00 Å^2	317.84 Å^2

For a more detailed comparison, the contributions of intermolecular contacts to the total Hirshfeld surface area were analyzed for several similar mononuclear copper(II) pyrazole-based complexes. The differences in the relative percentage contributions of elements to the total Hirshfeld surface area (Table 5) are attributed to the structural features of the studied compounds. The increased percentage contribution of nitrogen in "BACKEX" is explained by the absence of oxygen atoms and the presence of a cyano group in the structure of (3,5-dimethylpyrazolecarbimido)-cyanoamine. The increased contribution of intermolecular contacts involving hydrogen atoms in "VUCGIM" is due to the presence of an OH group positioned at the apex of the square pyramid. The difference in the globularity values of pyrazole-based complexes similar to $Cu(C_6H_8N_3O)_2$ falls within a range of 3.7 % to 5 %, while the asphericity values range from 15.3% to 22.5 % (Table 6). Higher globularity, lower asphericity, as well as the smallest molecular volume and surface area, indicate a more compact molecular shape of the complex [39].

Table 5

Relative percentage contributions of elements to the overall Hirshfeld surface for other mononuclear copper(II) pyrazole-based complexes

Interaction	The title compound	The compound with CCDC identifier BACKEX [38]	The compound with CCDC identifier VUCGIM [39]
Cu⋯all atoms	2.4	2.1	1.1
O⋯all atoms	10.9	-	2.0
H⋯all atoms	66.9	56.4	78.5
N⋯all atoms	9.3	27.7	7.7
C⋯all atoms	10.6	13.9	10.7

Table 6

The contributions of individual interactions to the overall Hirshfeld surface for other mononuclear copper(II) pyrazole-based complexes

Interaction or quantitative physical properties of the HS	The title compound	The compound with CCDC identifier BACKEX	The compound with CCDC identifier VUCGIM
Cu⋯Cu	0	0	0
Cu⋯N/N⋯Cu	0.7	3.2	0
Cu⋯C/C⋯Cu	2.5	0.7	0.8
Cu⋯O/O⋯Cu	0	-	0
Cu⋯H/H⋯Cu	1.2	0.2	0.3
N⋯N	1.5	1.6	1.1
N⋯C/C⋯N	3.1	4.4	2.5
N⋯O/O⋯N	0	-	1.7
N⋯H/H⋯N	11.5	40.5	5.6
C⋯C	0.9	1.2	0.4
C⋯O/O⋯C	0	-	3.5

Continuation of Table 2

C···H/H···C	12.1	18.3	7.8
O···O	0	-	0.4
O···H/H···O	19.5	-	38.3
H···H	47.0	29.8	37.7
Globularity	0.729	0.693	0.756
Asphericity	0.209	0.177	0.162
Molecular volume	327.50 Å^3	406.81 Å^3	308.79 Å^3
Surface area	315.07 Å^2	382.96 Å^2	292.06 Å^2

Conclusions

In this work, a method of oxidative dissolution was used to obtain mononuclear copper(II) complex $Cu(C_6H_8N_3O)_2$ with 1-carboxamide-3,5-dimethylpyrazole. Various techniques were used to identify and characterize the structure of complex $Cu(C_6H_8N_3O)_2$ and the ligand, such as IR and NMR spectroscopy, microanalyses, single-crystal X-ray diffraction. It was found that $Cu(C_6H_8N_3O)_2$ was formed as a result of a multistage process of oxidative dissolution of metallic copper with the participation of air oxygen and ammonium ions. This process leads to the appearance of a sufficient amount of Cu^{2+} ions in the solution, which partially ensures the production of the final compound, as well as the dissolution of zero-valent copper through the formation of intermediate Cu^{1+} compounds, which are oxidized by air oxygen to form divalent copper compounds. It has also been found that ammonium cyanate is formed in parallel through exchange reactions, which undergo dissociation in acetonitrile solutions, and the resulting HNCO undergoes hydrolysis. The hydrolysis products react with the starting ligand 3,5-dimethyl-1H-pyrazole to form 1-carboxamide-3,5-dimethylpyrazole. This acid then reacts with Cu^{2+} ions to form the final mononuclear complex $Cu(C_6H_8N_3O)_2$. The resulting mononuclear complex $Cu(C_6H_8N_3O)_2$ consists of almost planar molecules. The Cu^{II} ion displays a square-planar coordination environment formed by two pyridine-like nitrogen atoms and two carboxamide-like nitrogen atoms from two 1-carboxamide-3,5-dimethylpyrazole ligands coordinated in a bidentate chelating mode. In this case, they are located in a transposition to each other. The oxygen atoms O(1) and O(2) of the NCO group do not participate in the binding of Cu(II) atoms. Single-crystal X-ray diffraction analysis reveals that the title compound crystallizes in the triclinic crystal system, space group $P\bar{1}$ (Z = 2). The Hirshfeld surface analysis revealed that interactions involving hydrogen atoms (H···H, H···O/O···H, H···C/C···H, and H···N/N···H) dominate in the crystal packing of the title compound, with H···H contacts being the most significant. Comparisons with a polymorphic modification showed similar patterns, although there was a slight increase in H···H interactions and a decrease in H···O/O···H, H···N/N···H, and H···C/C···H contacts. Additionally, minor O···N/N···O and O···C/C···O interactions were detected, but their contributions were minimal. The molecular size and shape, represented by parameters like molecular volume, surface area, globularity, and asphericity, were nearly identical for the title compound and its polymorph. These results are consistent with data from similar complexes, showing negligible variation. The similarity in molecular volume, surface area, globularity, and asphericity values for comparable mononuclear copper(II) pyrazole-based complexes confirms their nearly identical molecular shape and size. The observed differences, particularly in the contributions of H···H, H···O/O···H, and other intermolecular contacts, are attributed to variations in the structural features of the ligands.

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