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SYNTHESIS, STRUCTURAL AND SPECTROSCOPIC CHARACTERIZATIONS, HIRSHFELD SURFACE ANALYSIS OF TWO COORDINATION COMPOUNDS ASSEMBLED FROM COPPER AND CARBOXYLATES, 3,5-DIMETHYL-1H-PYRAZOLE

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Abstract

Two coordination compounds $Cu(H_2O)(DMPZ)_2C_2O_4$ (1) (DMPZ = 3,5-dimethyl-1H-pyrazole) and $[Cu(H_2O)_2(CH_3COO)Br]_n$ (2) have been synthesized by oxidative dissolution method. The crystal structures of both compounds have been determined by single-crystal X-ray diffraction analysis. Complex 1 crystallizes in the triclinic $P\overline{1}$ space group, while complex 2 is orthorhombic crystals in the space group *Pnma.* In both compounds, the Cu(II) ion displays a slightly distorted square-pyramidal coordination environment. In complex 1, the coordination number of copper(II) ion is five, with the equatorial position formed by two nitrogen atoms belonging to the two monodentate coordinated 3,5-dimethyl-1H-pyrazole molecules, and two O atoms of the oxalate anion coordinated in a chelate mode. The axial position is occupied by the O atom of the water molecule. In complex 2, the copper equatorial surrounding consists of four oxygen atoms from two *trans*-disposed water molecules and two acetate groups that are bridged in *syn-anti* mode with neighboring copper atoms. The apical coordination site is occupied by the bromide ion. Elemental analysis and spectroscopy characterization of the complexes and 3,5-dimethyl-1H-pyrazole are also reported. The Hirshfeld surface analysis suggests that the main contribution to intermolecular interactions in both compounds comes from hydrogen bonds (H···O/O···H and H···Br/Br···H) and other close contacts involving hydrogen atoms.

Keywords: pyrazole ligands; copper complexes; carboxylates; X-ray crystallography; Hirshfeld surface analysis; coordination polymer.

СИНТЕЗ, КРИСТАЛІЧНА СТРУКТУРА, СПЕКТРАЛЬНІ ХАРАКТЕРИСТИКИ ТА АНАЛІЗ ПОВЕРХНІ ХІРШФЕЛЬДА КОМПЛЕКСІВ КУПРУМУ(ІІ) З КАРБОКСИЛАТАМИ, 3,5-ДИМЕТИЛ-1Н-ПІРАЗОЛОМ

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Анотація

Методом окисного розчинення (ОР) синтезовано моноядерний комплекс $Cu(H_2O)(DMPZ)_2C_2O_4$ (1) та координаційний полімер $[Cu(H_2O)_2(CH_3COO)_2Br]_n$ (2), встановлено їх будову за допомогою РСтА. При розчиненні порошку металічної міді у присутності DMPZ і солі амонію $(NH_4)_2C_2O_4$ та заданому співвідношенні метал:ліганд:сіль амонію 1 : 1 : 1 в ацетонітрилі отримали комплекс 1, що має молекулярну будову, а центральний атом Cu1 перебуває у викривленому тетрагонально-пірамідальному оточенні (O_2N_2O). Екваторіальна площина тетрагональної піраміди сформована з двох атомів оксигену від бідентатно-хелатно координованого оксалат-аніону та двох атомів нітрогену від недепротонованих монодентатно координованих молекул 3,5-диметил-1Н-піразолу. Апікальна позиція піраміди зайнята атомом оксигену від молекули води. У комплексі 2 центральний атом купруму перебуває у викривленому тетрагонально-пірамідальному оточенні (O_4Br). Екваторіальна площина поліедру атома Cu1 сформована з чотирьох атомів оксигену: два від бідентатно-містково *син-анти* координованих ацетатних-аніонів та два оксигени від молекул води. Аксіальна позиція Cu1 зайнята монодентатно координованим атомом брому. Відсутність у складі комплексу 2 піразолвмісного ліганду пояснюється наявністю в розчині додаткових лігандів конкуруючих із DMPZ, оскільки синтез здійснювали методом окисного розчинення металічного порошку купруму у присутності DMPZ і солей амонію (NH_4Br, NH_4OOCCH_3) та заданому співвідношенні метал : ліганд : сіль амонію 1 : 1 : 1 : 1 в розчині диметилформаміду. Отримані сполуки 1, 2 охарактеризовано за допомогою елементного аналізу, ІЧ-спектроскопії, а також приведено аналіз поверхні Хіршфельда для обох комплексів. Описано синтез ліганду (3,5-диметил-1Н-піразолу) та його ідентифікація за допомогою ЯМР, ІЧ-спектроскопії та елементного аналізу.

Ключові слова: піразоли; комплекси купруму; карбоксилати; РСтА; аналіз поверхні Хіршфельда; координаційний полімер.

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Introduction

Research on metal carboxylates has always been due to their important roles not only in synthetic chemistry, with the essence of the labile coordination modes of the carboxylate group, with architectures of open and porous frameworks [1–2], but also with regard to biological activities [3–4] and physiological effects [5–6]. The carboxylate groups can adopt a wide range of bonding modes, including monodentate, symmetric and asymmetric chelating, and bidentate and monodentate bridging [7–11].

Pyrazole ligands have been studied for over 40 years, as both neutral (Hpz) and anionic ligands (pz). In the neutral case, hydrogen bonding is usually observed together with metal coordination. The interplay of both phenomena is well known for many ligands, and certainly so for pyrazole compounds. This combination often can explain the formation and/or stability of the final structure of the coordination compounds [12–13].

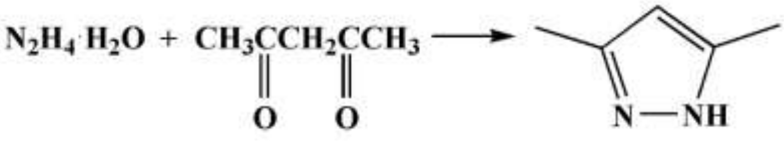
Various complexes containing pyrazole ligands have been synthesized and employed in coordination and organometallic chemistry [14–16]. Due to the presence of the N-N bridging function in the pyrazole ring, these ligands can form polynuclear complexes with specific molecular topologies. In this case, triangular azametallacrowns have been a much more common structure type [17–23]. Many complexes with simple pyrazole ligands, both in the terminal as well as bridging modes, are also available [24–32]. However, complexes based on carboxylic acids and pyrazole derivatives are not very common, except for some recently reported examples in the literature [33–36]. We have been working on coordination compounds with mixed ligands of carboxylate and pyrazole derivatives [37–39]. The pyrazole and carboxylate ligands appear to possess similar steric requirements and, to a certain extent, also similar bonding capabilities. In order to know the influence of the carboxylate anions on the formation of new complexes with pyrazole ligands and the role that weak non-covalent interactions play in forming the final supramolecular frameworks, we selected acetate and oxalate anions. Thus, in the following, we report the synthesis, structural characterization and Hirshfeld surface analysis of two Cu(II) complexes *via* a combination of 3,5-dimethylpyrazole (DMPZ) and different carboxylate ligands.

Although the X-ray structures of the title compounds were previously reported [40–41], we used another method for the preparation of **1** and **2**, namely the oxidative dissolution method (OD), in which metal powders are employed as starting materials. It has been shown to be an effective method for the production of both known and novel homo- and heterometallic polynuclear coordination compounds [14–17]. Often, unexpected and unpredictable complex formation processes take place under conditions of oxidative dissolution synthesis.

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}. ^1H NMR spectra were recorded on a Bruker AC-400 spectrometer (400 MHz) at room temperature. X-ray data were collected on a STOE IPDS II diffractometer (monochromated Mo-Kα radiation, λ = 0.71073 Å) by use of scans at low temperature. The structures were solved with SHELXT and refined on F^2 using all reflections with SHELXL [42]. Structure **2** was deposited at the Cambridge Crystallographic Data Centre (№ 2284149).

*Synthesis of 3,5-dimethyl-1H-pyrazole (**DMPZ**).* The synthesis of DMPZ 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 %. ^1H 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.



Scheme 1. Synthesis of 3,5-dimethyl-1H-pyrazole

*Synthesis of **1**.* Complex **1** was synthesized by reacting copper powder (0.64 g; 0.01 mol) with 3,5-dimethyl-1H-pyrazole (0.96 g; 0.01 mol) and ammonium oxalate (1.24 g; 0.01 mol) in 15 mL of acetonitrile solution in the presence of air oxygen. The mixture was stirred at room temperature until the solid completely dissolved. The resulting green solution was filtered, and the filtrate was left to stand in an open vessel at room temperature to allow for crystallization in air. The green crystals of compound **1** were formed within 4 days. Yield 85 %. Elemental analysis (%): calculated C, 39.77; H, 4.97; N, 15.47. Found: C, 39.75; H, 4.95; N, 15.44.

*Synthesis of **2**.* Complex **2** was synthesized using the oxidative dissolution method under free access of air oxygen. A mixture of 3,5-trimethyl-1H-pyrazole (0.48 g; 0.005 mol), ammonium acetate (0.385 g; 0.005 mol), and ammonium bromide (0.49 g; 0.005 mol) in 15 mL of dimethylformamide (DMF) solution was magnetically stirred with copper powder (0.32 g; 0.005 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 to allow for crystallization in an isopropanol solution. The blue needle-shaped crystals of compound **2**, suitable for X-ray analysis, were formed within 2 weeks. Yield 45 %. Elemental analysis (%): calculated C, 10.07; H, 2.95. Found: C, 10.00; H, 2.91.

Results and discussion

The formation of the title compound **1** (Fig. 1) proceeds according to the following scheme:

1) $Cu^0 + DMPZ + (NH_4)_2C_2O_4 + CH_3CN + O_2 \rightarrow Cu(H_2O)(DMPZ)_2C_2O_4 + NH_3 + H_2O$

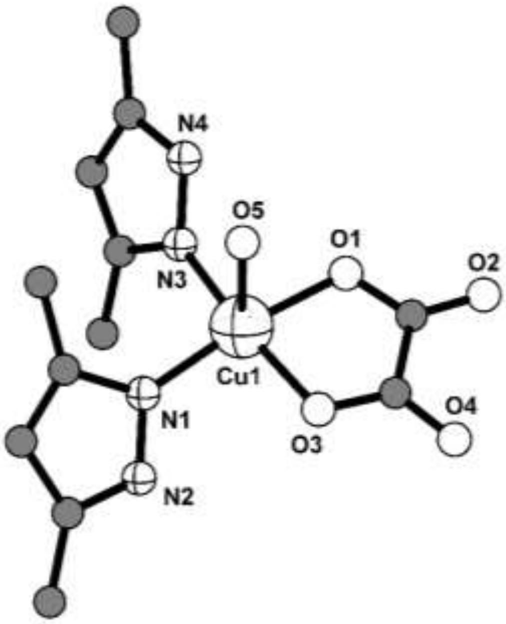


Fig. 1. The molecular structure of 1, shows the atom-numbering scheme and the copper coordination environment. H-atoms are omitted for clarity

Compound **1** has a molecular crystal structure, which consists of neutral monomeric $Cu(H_2O)(DMPZ)_2C_2O_4$ units. The Cu^{II} ion displays a slightly distorted square-pyramidal coordination environment (τ_5 = 0.037 [43]) formed by two pyridine-like nitrogen atoms of two DMPZ ligands coordinated in a monodentate mode, and two O atoms of the oxalate anion coordinated in a bidentate chelating mode in the equatorial positions. The axial position is occupied by the oxygen atom of the water molecule.

Unlike compound **1**, complex **2** (Fig. 2) does not contain molecules of 3,5-dimethyl-1H-pyrazole. This can be explained by the presence of additional ligands that compete with DMPZ in the solution. The formation of compound **2** proceeds according to the following scheme:

2) $Cu^0 + DMPZ + NH_4CH_3COO + NH_4Br + DMF + O_2 \rightarrow [Cu(H_2O)_2(CH_3COO)_2Br]_n + NH_3 + H_2O + DMPZ$

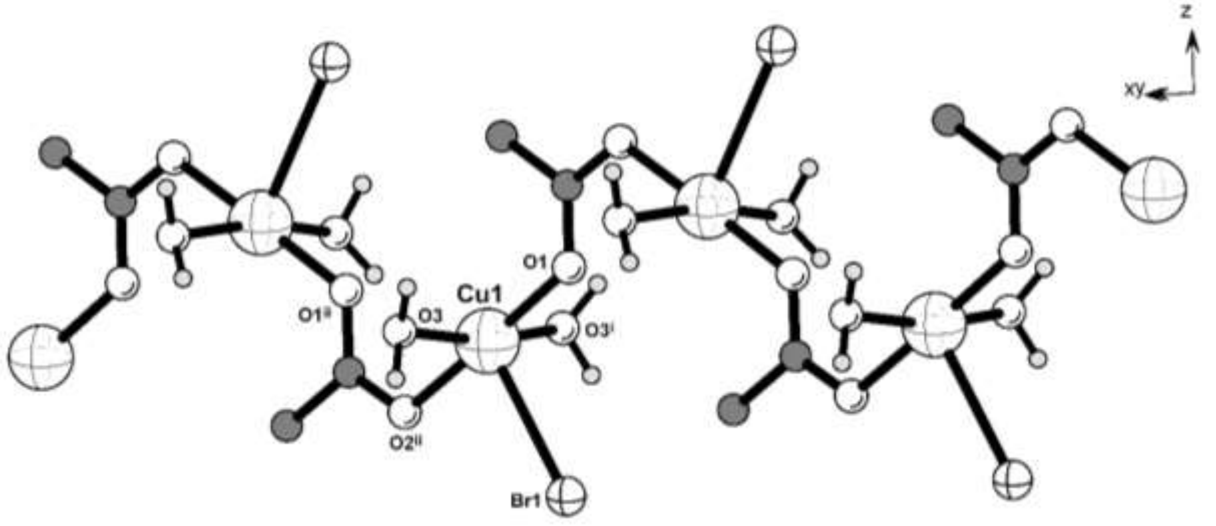


Fig. 2. The atom-numbering scheme of structure 2, the copper coordination environment and organization in the one-dimensiontional polymeric zigzag chain along the *x*-axis. [Symmetry codes: (i) -1+x, y, z; (ii) -1-x, 1-y, 2-z; (iii) -x, 1-y, 2-z; (iv) -2+x, y, z]

Compound **2** is a coordination polymer [$Cu(H_2O)_2(CH_3COO)_2Br]_n$, which crystallizes as orthorhombic crystals in the space group *Pnma.* The geometry of the five-coordinated Cu^{II} ion is a distorted square-pyramidal, with a geometry index τ_5 = 0.185 [43] (Figure 2). The copper equatorial surrounding consists of four oxygen atoms from two *trans*-disposed water molecules and two acetate groups. The apical coordination site is occupied by the bromide ion. The X-ray crystal structure showed that the copper ions were bridged by *syn-anti* acetate groups to form a one-dimensiontional polymeric zigzag chain along the *x*-axis. The intrachain and interchain distances between the copper(II) ions are 4.879 and 5.214 A, respectively.

Infrared spectra. The IR spectra of the complexes $Cu(H_2O)(DMPZ)_2C_2O_4$ (**1**) and $[Cu(H_2O)_2(CH_3COO)_2Br]_n$ (**2**) were recorded and analyzed (Fig. 3).

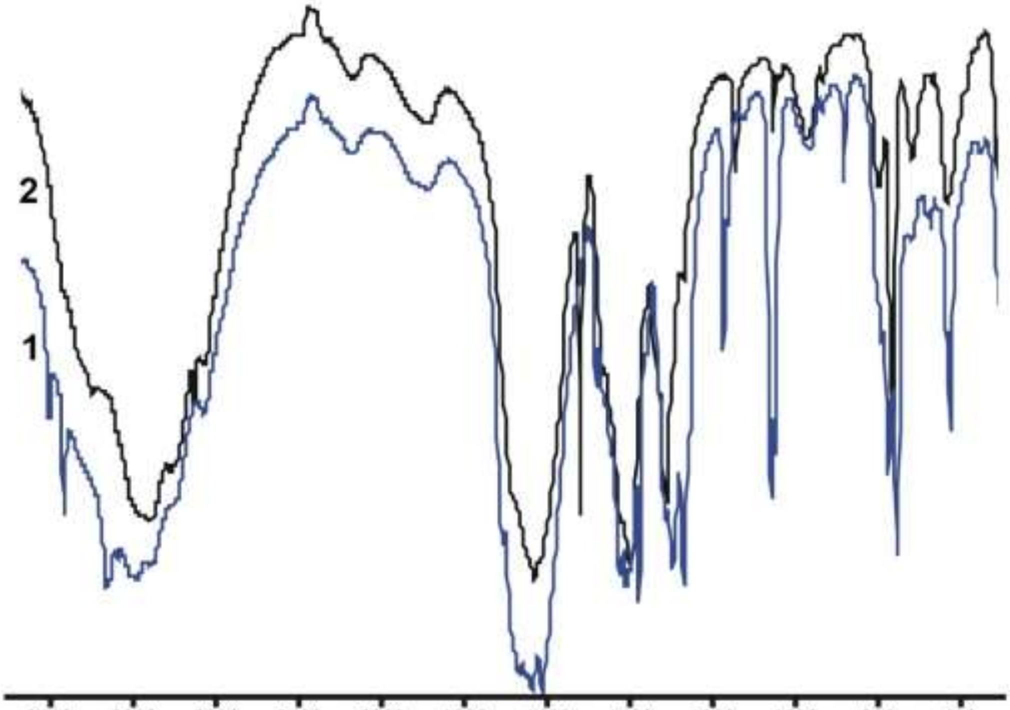


Fig. 3. IR spectra of the complexes $Cu(H_2O)(DMPZ)_2C_2O_4$ (1) and $[Cu(H_2O)_2(CH_3COO)_2Br]_n$ (2)

The ν(N–H) and ν(C–H, aliphatic) stretching vibrations of the 3,5-dimethyl-1H-pyrazole are observed as multiple bands in the region at 2800-3500 cm^{-1}. The other absorption peaks of the ligand DMPZ appear at 1700-650 cm^{-1}. In both complexes, a narrow intense band at 1620 cm^{-1} (for **1**) and 1600 cm^{-1}(for **2**) (δ(MOH)) and a multiplet of narrow bands in the region of 3160–3240 cm^{-1}, which can be attributed to ν(OH), indicate the presence of water molecules. In complex **2**, weak bands due to the acetate methyl groups C–H stretching vibrations are identified at 2800–2900 cm^{-1}. The acetate ions give rise to two strong bands in the spectra of **2**: an asymmetric (ν_{as}) stretching band at 1570 cm^{-1} and a symmetric (ν_s) stretching band at 1440 cm^{-1}. The difference in wavenumbers, Δ=130 cm^{-1}, between the ν_{as} and ν_s COO$^-$ stretching frequencies indicates the presence of bridging acetate ligands [44], in line with the X-ray structure determination. The oxalate anion coordinates to a copper (**1**) in a bidentate chelating mode and exhibits the vibrational modes ν_{as}(CO), ν_s(CO), and δ(OCO) at 1688, 1368, and 790 cm^{-1}, respectively [44].

Hirshfeld surface analysis. The Hirshfeld surface analysis and the associated two-dimensional fingerprint plots were performed using Crystal Explorer 17.5 software [45] for complex **1**, with a standard resolution of the three-dimensional d_{norm} surfaces plotted over a fixed colour scale of -0.5963 (red) to 1.1404 (blue) a.u. There are 19 red spots on the d_{norm} surface (Fig. 4). The dark-red spots correspond to short interatomic contacts and represent negative d_{norm} values on the surface, while the other weaker intermolecular interactions appear as light-red spots. The Hirshfeld surfaces mapped over d_{norm} are shown for the H···H (49.1 %), H···O/O···H (30.7 %), H···C/C···H (8.9 %), H···N/N···H (4.9 %) and C···O/O···C (3.1 %) contacts, the overall two-dimensional fingerprint plot and the decomposed two-dimensional fingerprint plots are given in Fig. 5. The small contribution of the other weak intermolecular O···O (1.3 %), C···C (0.8 %), Cu···O/O···Cu (0.8 %) and N···O/O···N (0.3 %) 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 (69.5 %), O···all atoms (19.6 %), C···all atoms (7.8 %), N···all atoms (2.6 %) and Cu···all atoms (0.5 %). Additionally, quantitative physical properties of the Hirshfeld surface for this compound were obtained, such as molecular volume (357.56 Å^3), surface area (332.16 Å^2), globularity (0.733), and asphericity (0.069).

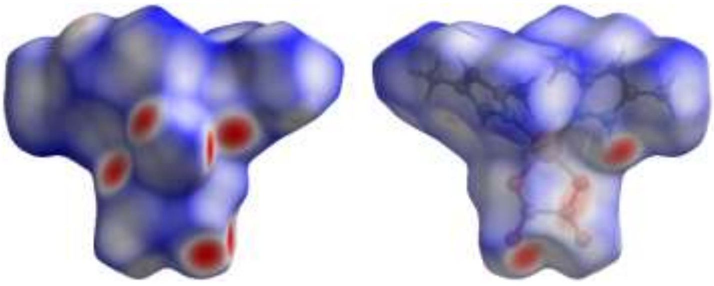


Fig. 4. Two projections of Hirshfeld surfaces mapped over d_{norm} showing the intermolecular interactions within the molecule.

For complex 2, the Hirshfeld surface analysis and the associated two-dimensional fingerprint plots were also performed with a standard resolution of the three-dimensional dnorm surfaces plotted over a fixed colour scale of –1.5176 (red) to 1.2257 (blue) a.u. There are 13 red spots on the dnorm surface (Fig. 6). The Hirshfeld surfaces mapped over dnorm are shown for the H···H (41.1%), H···Br/Br···H (23.5 %), H···O/O···H (15.9 %), Cu···O/O···Cu (6.1 %), O···O (6.1 %) and Br···O/O···Br (5 %) contacts, the overall two-dimensional fingerprint plot and the decomposed two-dimensional fingerprint plots are given in Fig. 7. The small contribution of the other weak intermolecular Br···C/C···Br (1.3 %), C···O/O···C (0.5 %), H···C/C···H (0.4 %) and H···Cu/Cu···H (0.1 %) contacts have a negligible effect on the packing. The relative percentage contributions to the overall Hirshfeld surface by elements: H···all atoms (52.1 %), Br···all atoms (22.1 %), O···all atoms (21.3 %), Cu···all atoms (3.3 %) and C···all atoms (1.2 %). Also, quantitative physical properties of the Hirshfeld surface for complex 2 were obtained, such as molecular volume (159.80 Å^3), surface area (185.47 Å^2), globularity (0.768), and asphericity (0.113).

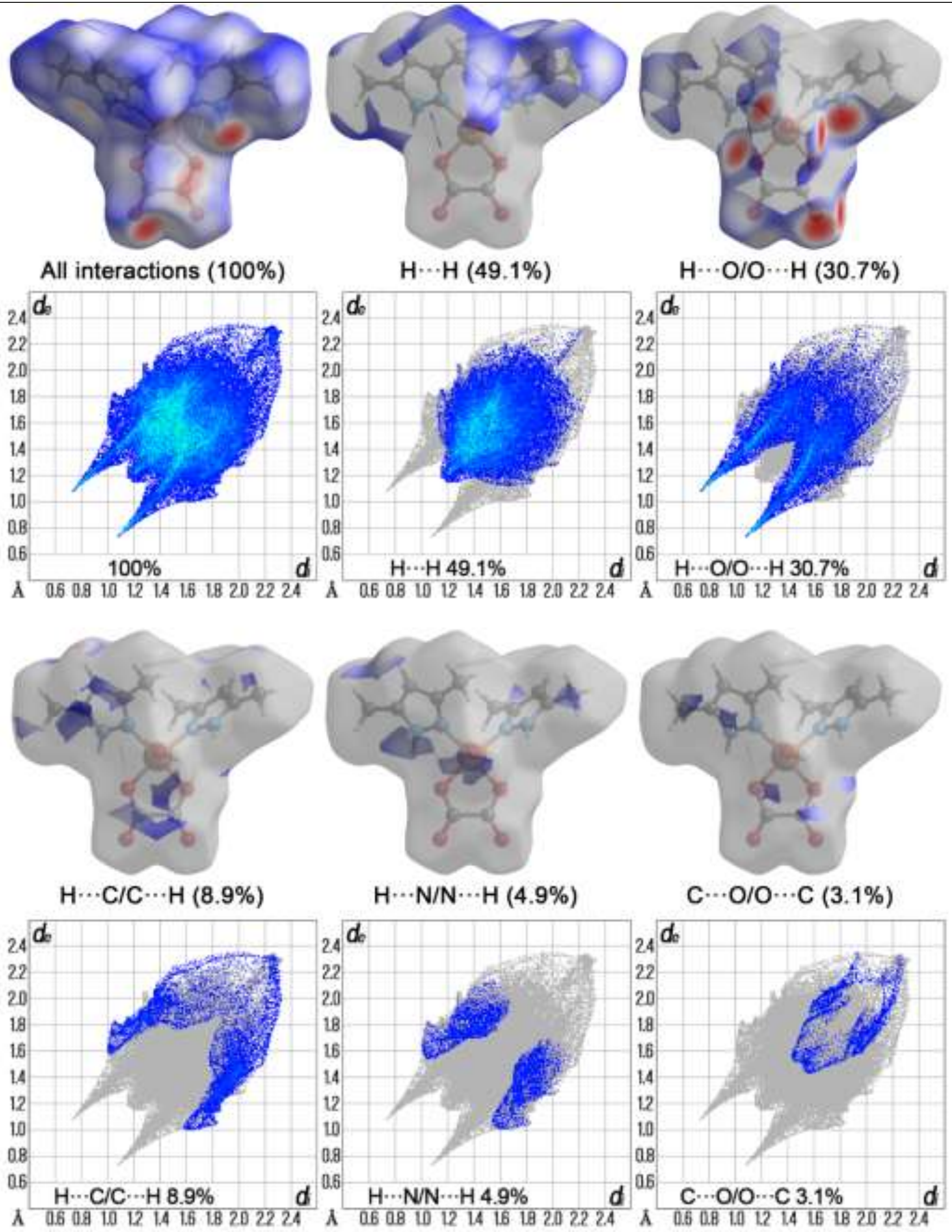


Fig. 5. The overall two-dimensional fingerprint plot and those delineated into specified interactions. Hirshfeld surface representations with the function d_{norm} plotted onto the surface for the different interactions.

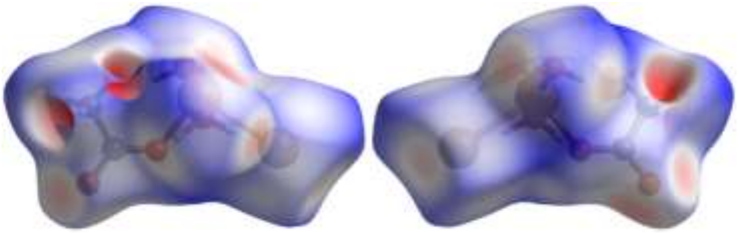


Fig. 6. Two projections of Hirshfeld surfaces mapped over d_{norm} showing the intermolecular interactions within the molecule.

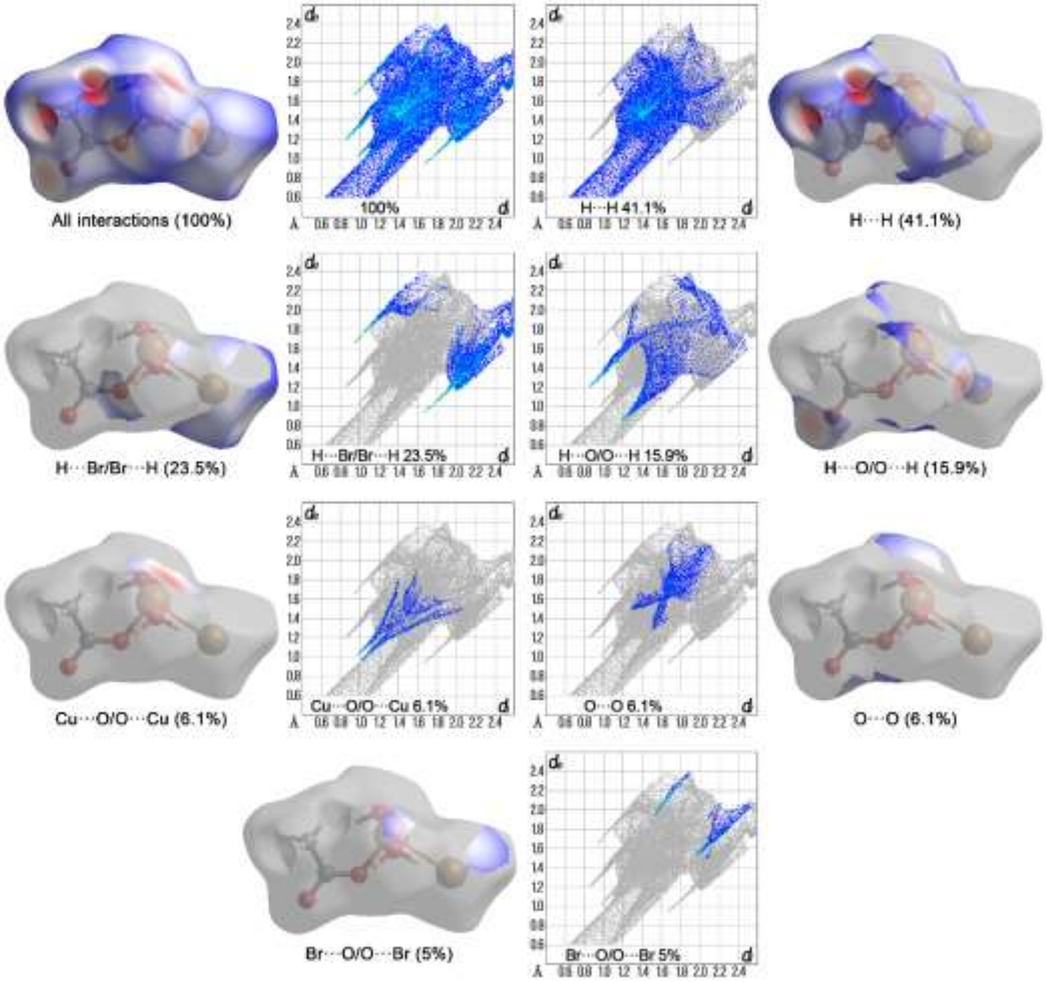


Fig. 7. The overall two-dimensional fingerprint plot and those delineated into specified interactions. Hirshfeld surface representations with the function d_{norm} plotted onto the surface for the different interactions.

Conclusions

The present report describes the synthesis and characterization of two coordination compounds: a mononuclear complex $Cu(H_2O)(DMPZ)_2C_2O_4$ and a coordination polymer $[Cu(H_2O)_2(CH_3COO)_2Br]_n$ consisting of monomer units. Single crystal X-ray analysis reveals a slightly distorted square-pyramidal geometry of the central Cu^{II} atom in both complexes. In the case of the compound $Cu(H_2O)(DMPZ)_2C_2O_4$ the four equatorial positions are occupied by two N atoms belonging to the two monodentate coordinated 3,5-dimethyl-1*H*-pyrazole molecules and two O atoms of the oxalate anion coordinated in a chelate mode, forming a five-membered chelate ring. The axial position is occupied by the O atom of the water molecule. In contrast to the above-mentioned compound, the complex $[Cu(H_2O)_2(CH_3COO)_2Br]_n$ does not include the molecules of 3,5-dimethyl-1H-pyrazole, which can be explained by the presence of additional ligands competing with DMPZ in the solution. The copper(II) atom is five-coordinated, and the equatorial plane is composed of four oxygen atoms (two water and two neighboring acetate groups). The apical coordination site is occupied by the bromide ion. Elemental analysis and spectroscopy characterization of the obtained complexes and ligand (3,5-dimethyl-1H-pyrazole) are also reported. The coordination mode of ligands was established by IR spectroscopy: the oxalate anion has a bidentate chelating coordination mode, and the acetate groups are bridging *syn-anti.* According to the Hirshfeld surface analysis, hydrogen bonds (H···O/O···H and H···Br/Br···H) and other close contacts involving hydrogen atoms make the main contribution to intermolecular interactions in both compounds.

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