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PHYSICO-CHEMICAL STUDIES OF MONO-AQUA-COORDINATED COPPER-BASED BIS(HYDROXYNAPHTHALDEHYDE) COMPLEX

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Abstract. A new metallocomplex compound containing [Cu(2-hnaf)$_2$H$_2$O] was synthesized from the interaction of solutions of 2-hydroxy 1-naphthaldehyde (2-hnaf) with $CuSO_4$ in ethyl alcohol. The composition, molecular and crystal structures of this metallocomplex compound were investigated using differential scanning calorimetry (DSC), IR-spectrum and X-ray structure analysis (XRSA). It was found that the thermal decomposition of the organic part of the metal complex in the DSC-analysis is different, starting from 115°C and ending in the temperature range of 370°C. The data obtained in the XRSA analysis also proved the presence of coordination water molecules. Based on the obtained data, the Hirshfeld surface analysis of the complex was studied. The results of the surface analysis revealed that the main part of the effects are H...O/O...H, H...H and H...C/C...H interactions that contribute the most to the Hirshfeld surface. The complex contains H…C/C…H (45.3%), H…H (34.7%) and H…O/O…H (11.8%), which is expected for molecules dominated by oxygen atoms.

Keywords: *2-hydroxy 1-naphthaldehyde, copper (II) sulfate, ethyl alcohol, coordination water, Hirshfeld.*

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1. Introduction

Currently, representatives of the medical field are seriously fighting against diseases affecting human health (cancer, AIDS and other chronic inflammations). In this direction, representatives of the chemical and pharmaceutical fields are doing a number of things in order to create a new drug and achieve its effective effect even in micro doses.

Along with natural medicinal preparations, synthetic medicinal preparations are also being used effectively in medical practice. From several intermediates, new biologically active substances with significant efficacy can be synthesized. In this case, due to the phenomenon of synergism, the toxicity may decrease and the beneficial properties may increase. Taking these circumstances into account, we aimed to synthesize mixed ligand complexes of *2-hydroxy-1-naphthaldehyde* with bioactive metals and study their physicochemical properties.

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It is known from the literature that mixed ligand metallocomplexes of ligand: *2-hnaf* with Cu metal were synthesized and their activity against cancer cells was studied (Gonzalez-Alvarez *et al*., 2003; Kathiresan *et al*., 2016). Medicinal products containing copper metal are of interest in medicine due to their flexibility compared to platinum and non-platinum anticancer agents and their much lower toxicity to normal tissues. In addition, a number of scientists (Eshkurbonov & Rakhmonkulov, 2022) have synthesized ionites that form selective complexes with non-ferrous and precious metals and these ionites are isolated from solutions by forming coordination bonds with small amounts of non-ferrous and precious metal ions (Eshqurbonov & Safarova, 2023). The synthesis, sorption properties and absorption kinetics of these compounds have been studied using IR spectroscopy and electron microscopy (Eshkurbonov & Safarova, 2024). The conditions of synthesis of new water-soluble metallocomplexes of *2-hnaf* with other biologically active metals were studied and their molecular structures were studied based on X-ray structure analysis (XRSA) (Gupta *et al*., 2013; Liang *et al*., 2010). Metal clusters of *2-hnaf* were obtained and their physical and chemical properties were studied (Adam *et al*., 2019; Ma *et al*., 2013). In this work, the synthesis, thermal (DSC), IR-spectrum, XRSA and Hirshfeld surface analyzes of the metallocomplex compound of *2-hnaf* with copper metal are presented.

Methanol was used as a solvent to obtain a tetragonal pyramidal complex with copper metal, that is, for synthesis, the salt $Cu(NO_3)_2$ and 2-hydroxy-1-naphthaldehyde were dissolved in methanol and mixed to synthesize the complex compound (Parveen *et al*., 2020).

2. Experimental part

2.1. Chemicals, instruments and calculation

All reagents were obtained from commercial sources and used without purification. Determination of the structure of the crystal was carried out by Oxford diffraction Xcalibur-R CCD (CuKa,- radiation, λ=1.54184 Å, ω - scanning mode, graphite monochromator (at 293K)) (Xcalibur, 2009. The structure was obtained using the SHYeLX-97 software package (Sheldrick, 1997). Molecular drawings were obtained by the MERCURY software package (Macrae *et al*., 2008).

2.2. Synthesis of complex compound

In this experiment, our scientific team took into account the low solubility of 2-hydroxy-1-naphthaldehyde in water and the reactants were dissolved in ethyl alcohol. When mixing 2-hydroxy-1-naphthaldehyde and copper (II) sulfate pentahydrate in ethyl alcohol in a stoichiometric ratio of 2:1, an opaque solution was obtained. In order to clarify the solution, it was mixed in a mechanical mixer for 40-45 minutes at 35-40°C until a green transparent solution was obtained. The resulting solution was left to evaporate at room temperature with the mouthpiece not fully closed. After about 7-10 days, green crystals formed. The formed crystals were washed with ethyl alcohol. Product yield is 80%, element analysis (C) = 62.26%, (O_2) = 18.77%, (Cu) = 15.1%. (H_2)=3.77% were found. When the single crystals suitable for examination in XRSA were selected and examined, it was found that the composition is mono aqua chelate complex with [Cu(*2-hnaf*)$_2$$H_2O$]. The reaction equation of the synthesized complex was proposed as follows (Figure 1)

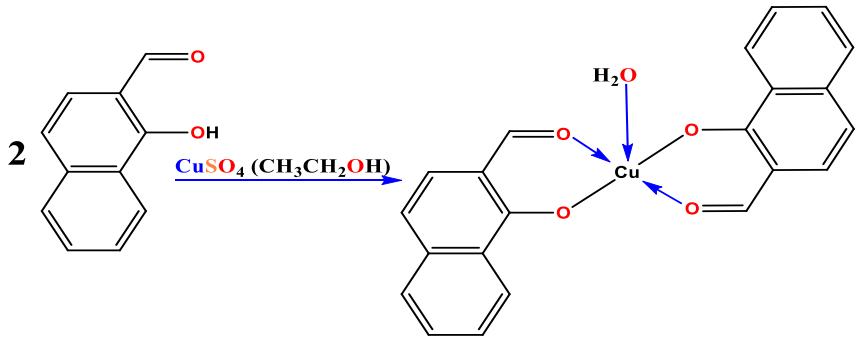

Figure 1. Synthesis scheme of [Cu(*2-hnaf*)$_2$ H_2O] complex

3. Results and Discussions

When studying the melting temperatures, it was found that the formed complex melts at a higher temperature (208.7°C) than the ligand (134.3°C). In order to study the thermal nature of the obtained complex crystal form, DSC analysis was conducted (Figure 2).

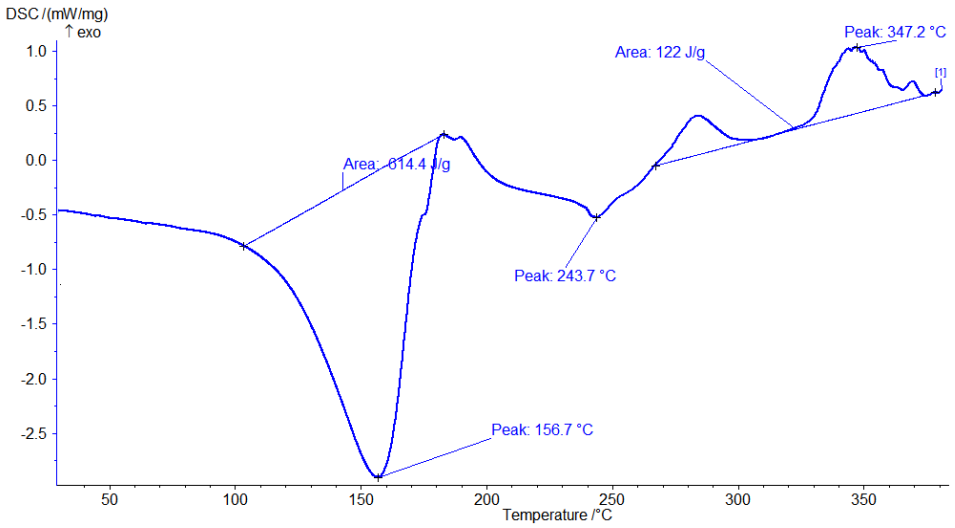

Figure 2. DSC analysis of the complex obtained on the basis of copper (II) sulfate and *2-hnaf*

It was found that the thermal decomposition of the organic part of the complex is different, starting from 115°C and ending in the temperature range of 370°C. DSC curves are explained by endo - and exo - effects, which mean the breaking of previous chemical bonds and the formation of new ones in this process. According to the results, the nature of the DSC curves for the obtained complex is the same. The first DSC curves of the complex were observed with an endothermic effect at 156.7°C and ΔQ = - 614.4 J/g and the second curves with an endothermic effect at 243.7°C and ΔQ = -122 J/g. If the endothermic effect at 156.7°C is explained by the separation of coordination water, the endothermic effect at 243.7°C leads to the liquefaction and subsequent decomposition of the substance. Based on the analysis of the research results, it was determined that water is located in the inner sphere of the complex compound. It was concluded that the complex compound synthesized on the basis of *2-hnaf is an aqua complex.*

2- hnaf and when the IR-spectra of the obtained complex was studied, it was found that the IR-spectra of *2-hnaf* is the same as the information given in the literature. When the IR-spectrum of the complex was studied, it was found that there are absorption lines characteristic of additional functional groups. It was found that the absorption line (1645 cm^{-1}) caused by the valence vibrations of the C=O group in the free ligand molecule shifted to a lower frequency range in the spectra of the complex. It is known that the asymmetric ν_{as} (C=O) vibrations of the carbonyl (C=O) group are observed in the area above 1600 cm^{-1}, while the symmetric ν_s (C=O) vibrations are observed in the lower area (1366, 1439). The presence of wavy or sail-like absorption lines in the 3300-3600 cm^{-1} areas of the complex compound indicates the presence of coordination water molecules (Figure 3).

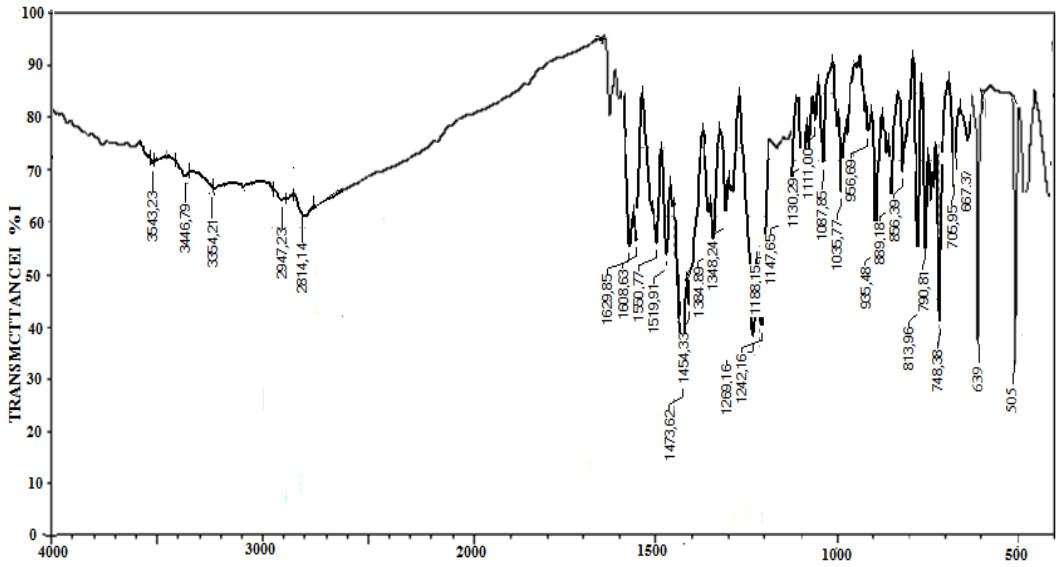

Figure 3. IR-spectrum of the complex compound obtained on the basis of copper (II) sulfate and *2-hnaf*

In the IR-spectrum of the complex compound in Figure 3 above, the appearance of new absorption lines characteristic of coordination water in the region of 3300-3600 cm^{-1} and the observation of changes in the absorption lines characteristic of existing groups indicate the formation of a complex compound.

We have summarized the information about the absorption lines observed in the IR-spectrum of the obtained complex compounds in Table 1.

Table 1. IR-spectra of ligand and complex compounds

Vibration description → / **Ligand and complex ↓**	**H_2O**	**A_r(=CH)**	**ν_{as} (C=O)/ ν_s (C=O)**
2- hnaf	-	3054, 2957, 864	1645, 1439, 13 66
[Cu(*2-hnaf*)$_2$ H_2O]	3300-3600	2947, 866, 814	1629, 1608, 1454, 1384

Changes in the melting temperatures of the ligand and the obtained complex compound, the results of DSC and IR-spectroscopic analyzes can be concluded that a metallocomplex compound was obtained based on copper (II) sulfate and *2-hnaf*.

When the molecular and crystal structure of the synthesized metallocomplex compound was studied using XRSA, the data from the above DSC analysis and IR-spectrum analysis were fully confirmed and the composition of the synthesized complex [Cu(*2-hnaf*)$_2$H$_2$O] proved to be. It was determined that the complex compound is a mononuclear mixed-ligand aquacomplex and its molecular and crystal structure was studied (Fig. 4).

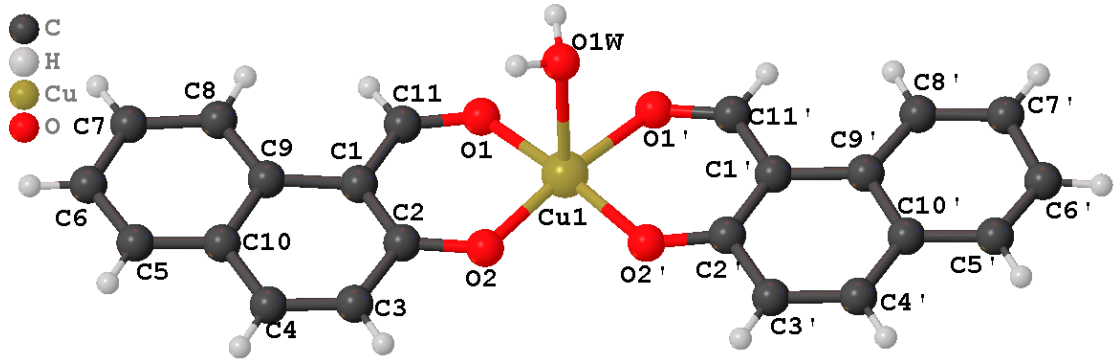

Figure 4. Molecular structure of the [Cu(*2-hnaf*)$_2$H$_2$O] complex

In the resulting complex, the central atomic polyhedral has a tetragonal pyramidal structure and is hybridized in the sp^3d state. In the complex compound, *2-hnaf* binds to the central atom as a bidentate ligand, causing the formation of a chelate complex with a six-membered ring. *2-hnaf* is bonded to the central atom through the oxygen atoms. The O1-Cu1 and O2-Cu bonds are connected at a distance of 1.932 and 1.894 Å, respectively. In the complex compound, the second *2-hnaf* is also bonded to the central atom in a bidentate position and the O1'-Cu1 and O2'-Cu1 bonds are 1.944 and 1.933 Å, respectively. Based on the ligand field theory, one water molecule is coordinated as a monodentate ligand in order to saturate the main and additional valences of the central atom. The same water molecule connected with the central atom (O1w-Cu1 2.336 Å) and formed the apex of the tetragonal pyramid. Looking at the bond lengths, we can see that there is a mismatch in the lengths of the five metal-oxygen bonds. When this state is Cu^{+2}, the electronic configuration becomes $3d^9$, as a result, Jan-Teller effect is observed in complexes with tetragonal pyramid and octahedron structure.

The structure of the obtained complex compound was analyzed by EPR spectroscopy, mass spectroscopy and UV spectroscopy. The biological activity of this obtained complex was studied on the basis of both theoretical and practical experiments against DNA and RNA nucleic acids (Parveen *et al*., 2020). This complex compound was synthesized by our scientific team and we aimed to study its unanalyzed physico-chemical research. Based on the XRSA data of the obtained complex compound, Hirshfeld surface analysis was performed using Crystal Explorer17.5 software (Turner *et al*., 2017). Hirshfeld surface analysis d_{norm} area volume 429.62 Å^3, the surface is 393.28 Å^2 at, dimensions -0.2993 (red) 1.3159 (blue) was seen and determined external (d_e) and internal (d_i) distances by calculating to the nearest nucleus. On the Hirshfeld surface, the points with a low impact contribution are shown in blue and the points with a high impact contribution are shown in red (Figure 5a). Analysis of the two-dimensional fingerprint domain plots revealed that H…O/O…H, H…H and H…C/C…H interactions contribute the most to the Hirshfeld surface. The complex contains H…C/C…H (45.3%), H…H

(34.7%) and H…O/O…H (11.8%), which is expected for molecules dominated by oxygen atoms (Figure 6).

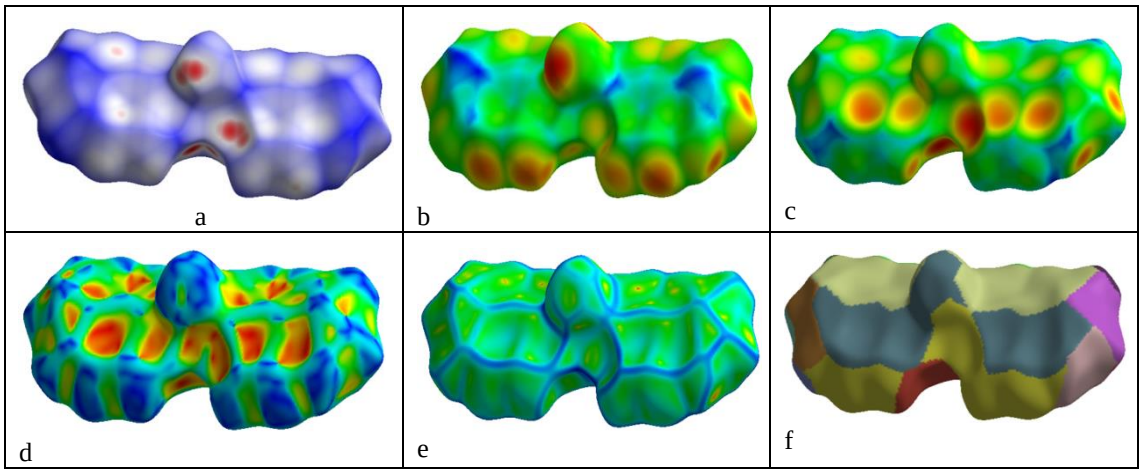

Figure 5. Image of the surface properties of the Hirshfeld surface analysis of the complex compound containing $[Cu(2\text{-hnaf})_2H_2O]$: (a) d_{norm}; (b) d_i; (c) d_e; (d) shape-index; (e) Curvedness; (f) Subdivision

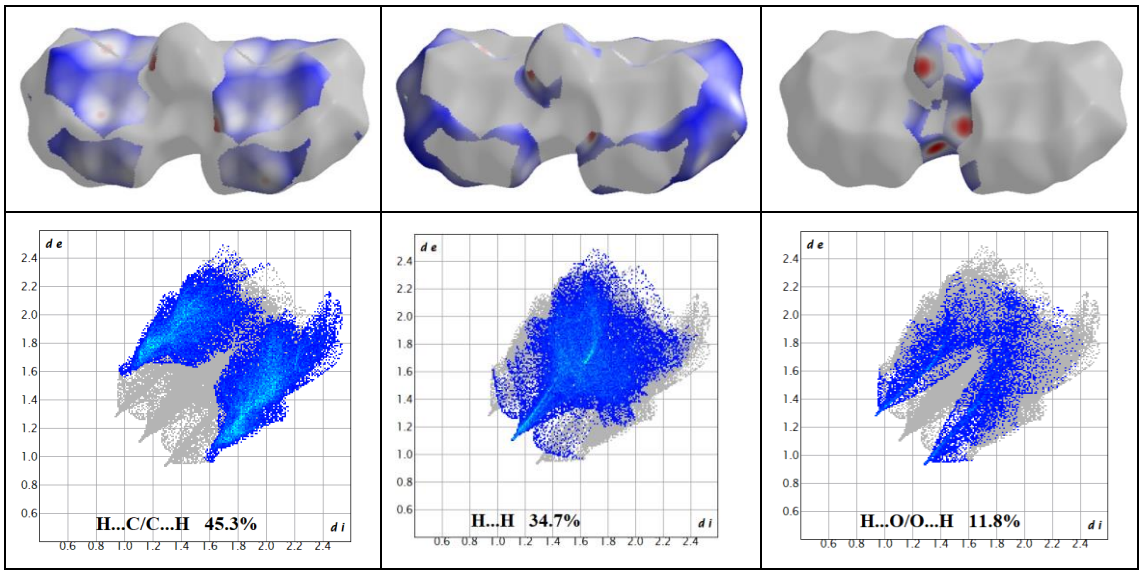

Figure 6. Three-dimensional Hirshfeld surface and two-dimensional fingerprint area mapped according to the d_{norm} representing interactions H…C/C…H, H…H and H…O/O…H in the $[Cu(2\text{-}hnaf)_2H_2O]$ complex crystal

Of the remaining interactions in the complex compound, the effects of, O...O(4.7%), O...C/C...O(1.9%), Cu...O/O...Cu (1.5%) are also significant and H...Cu/Cu…H (0.1%) the contribution of effects is less (Figure 7).

This complex compound contains intramolecular and intermolecular hydrogen bonds of the N−H---O and O−H---O types. In the internal hydrogen bond of the molecule, it occurs between the hydroxyl (OH) group attached to the second carbon atom and the second oxygen atom in the carboxyl group (O3−H3---O2). Intermolecular hydrogen bonds occur between the OH group attached to the fourth carbon atom and the first oxygen atom in the carboxyl group of the side molecule (O4−H4---O1).

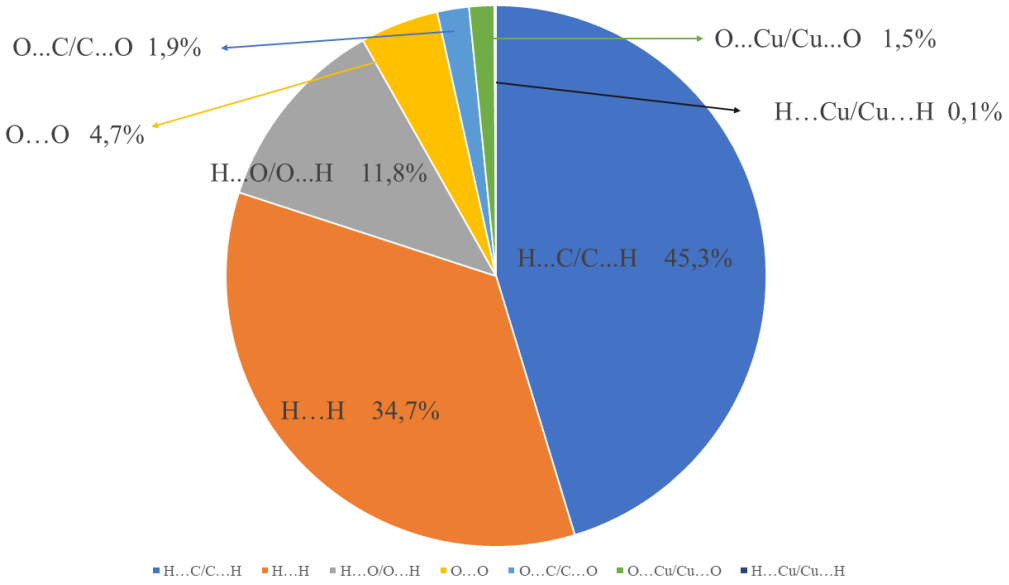

Figure 7. Hirshfeld fingerprint diagram of the complex [Cu*(2-hnaf)*$_2$H$_2$O]

In addition, the molecule contains internal hydrogen bonds such as N1−H1A---O1, N2−H2A---O1 and N2−H2B---O1.

4. Conclusion

As a result of the research conducted, for the first time, *2-hnaf* with copper (II) sulfate a complex compound was synthesized. The composition, molecular and crystal structures of the complex compound were determined using DSC analysis, IR-spectrum and XRSA. The resulting complex compound was obtained from the Cambridge Crystallographic Data Center under the corresponding deposit reference number 2395105. It was determined that the Jan-Teller effect is observed due to the $3d^9$ configuration of the Cu^{+2} ion. In the Hirshfeld surface analysis, it was found that H...C/C...H (45.3%) , H...H (34.7%) and H...O/O...H (11.8%) constitute the main part of the effects.

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