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SYNTHESIS, STRUCTURE AND HIRSHFELD SURFACE ANALYSIS OF THE METAL COMPLEX FORMED BY CLUSTER-TYPE 2-HYDROXY-1-NAPHTHALDEHYDE WITH Zn^{2+} ION

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Abstract. A new metal complex compound $[Zn_2(2\text{-}hnaf)_2(NO_3)_2(H_2O)_2]$ was synthesized by the reaction between solutions of 2-hydroxy-1-naphthaldehyde *(2-hnaf)* and $Zn(NO_3)_2{\cdot}3H_2O$ in ethyl alcohol. The composition, molecular and crystal structures of this metal complex compound were investigated using X-ray structural analysis (XRD). The data obtained from XRD analysis also confirmed the presence of coordinated water molecules. *2-hnaf* is bound to the central atom via oxygen atoms. Bond lengths OA1-ZnA1, OA2-ZnA1 and OA2-ZnB1 (as well as bond lengths OB1-ZnB1, OB2-ZnB1 and OB2-ZnA1) are 2.051, 2.012 and 2.073 Å, respectively. In the complex compound, the nitrate anion is also bidentately bonded to the central atom, with each ligand having two rings, forming a chelate with a total of four membered rings. Based on the obtained data, the Hirshfeld surface analysis of the complex was studied. The results of the surface analysis revealed that the majority of interactions are H...O/O...H (35.8%), H...H (24.3%), H...C/C...H (23.3%), C...C (6.3%) and O...O (4.4%).

Keywords: *2-hydroxy-1-naphthaldehyde, zinc nitrate trihydrate, ethyl alcohol, mixed-ligand, bond lengths, Hirshfeld, XRD.*

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1. Introduction

Currently, the resistance of microorganisms to antibiotics is emerging as a serious medical problem on a global scale. The resistance of microorganisms to antibiotics significantly complicates the treatment of infections. Resistant strains overburden the healthcare system, increase the risk of death and reduce the effectiveness of medical procedures such as surgery and cancer treatment. Therefore, it is necessary to develop effective antimicrobial therapies, as well as optimize existing antibiotics using the chelation process (Lutgring *et al*., 2017). It is possible to synthesize new biologically active substances with significant effectiveness from several intermediate substances. In this case, due to the phenomenon of synergism, toxicity may decrease while beneficial properties may increase. Taking these circumstances into account, we aimed to synthesize mixed-ligand chelate complex compounds of 2-hydroxy-1-naphthaldehyde with bioactive metals and study their physicochemical properties.

Authors report that 2-hydroxy-1-naphthaldehyde *(2-hnaf)* is used as an intermediate product in organic synthesis, as an analytical reagent for the determination

of palladium and beryllium and in the synthesis of adipic dihydrazones with antibacterial activity (Fernández & Espinosa, 1994). In medical practice, it is used for synthesizing drugs that inhibit bacterial cells (Parveen *et al*., 2020). Mixed-ligand chelate complexes *of 2-hnaf* with Cu metal were synthesized and their anti-cancer activity was studied (Jayamani *et al*., 2018). Literature reports the synthesis conditions of a new water-soluble metal complex *of 2-hnaf* with biologically active metals, as well as its molecular structure determined by X-ray structural analysis (XRD) (Eshkurbonov *et al*., 2025). Metal clusters *of 2-hnaf* have also been obtained and their physicochemical properties studied (Tziotzi *et al*., 2016). This work presents the synthesis of a new chelate complex compound *of 2-hnaf* with zinc metal, along with XRD and Hirshfeld surface analyses.

2. Experimental

2.1. Research Methodology

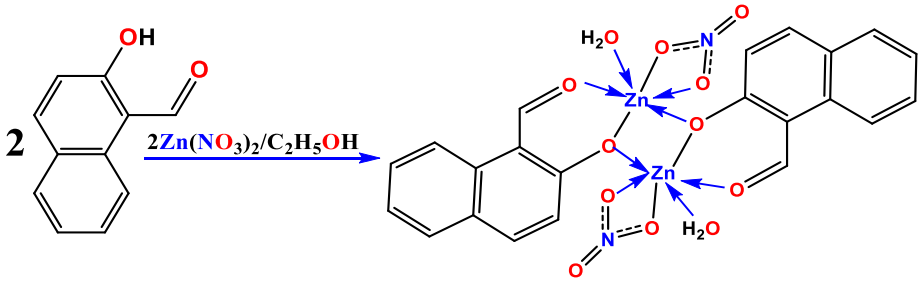
All reagents were obtained from Company "Sigma-Aldrich" and used without purification. Crystal structure determination was carried out using an Oxford Diffraction Xcalibur-R CCD (CuKα radiation, λ=1.54184 Å, ω-scanning mode, graphite monochromator at 293K) (Xcalibur, 2009). The structure was solved using the SHELX-97 software package (Sheldrick, 1997). Molecular drawings were generated using the MERCURY software package (Macrae *et al*., 2008).

2.2. Synthesis of new complex

In this experiment, considering the low solubility of 2-hydroxy-1-naphthaldehyde *(2-hnaf)* in water, the reagents for the reaction were dissolved in 96% ethyl alcohol. A clear solution was prepared by dissolving the ligand *2-hnaf* (0.2 mmol = 0.0344 mg) in 5 ml of this solvent. $Zn(NO_3)_2 \cdot 3H_2O$ (0.2 mmol = 0.0486 mg) was dissolved in ethanol to obtain a clear solution. The solutions were mixed in a 1:1 molar ratio (2-hnaf: $Zn(NO_3)_2 \cdot 3H_2O$) and the resulting mixture was heated and stirred in a mechanical stirrer for 30-35 minutes at a temperature of 40-45°C until the solution became clear. The newly formed solution was left for evaporation at room temperature with the container partially opened. After approximately 8-10 days, colorless crystals were formed. The resulting crystals were washed with ethyl alcohol.

2.3. Characterization of new compound

When studying the melting temperatures of the obtained single crystals, it was found that the resulting complex melted at a higher temperature (218.9°C) compared to the ligand (134.3°C). The molecular and crystal structure of the synthesized metal complex compound was studied using X-ray diffraction analysis, which proved that the composition of the complex is $[Zn_2(2\text{-}hnaf)_2(NO_3)_2(H_2O)_2]$. The reaction equation for the synthesized single crystal was proposed as shown in Scheme 1.



Scheme 1. Synthesis of the $[Zn_2(2\text{-}hnaf)_2(NO_3)_2(H_2O)_2]$ complex

2.4. The crystal's unit cell parameters

The synthesized metal complex compound of [Zn_2*(2-hnaf)*$_2$ (NO_3)$_2$ (H_2O)$_2$] composition, *containing 2-hnaf* and Zn (II). The crystal's unit cell parameters are as follows: monoclinic crystal system, space group *P21/c*, V=1197.13 Å3, Z=1. It was established that the obtained complex compound is a new chelate complex compound with mixed ligands of the binuclear cluster type. Its molecular and crystal structure were studied (Figures 1-2).

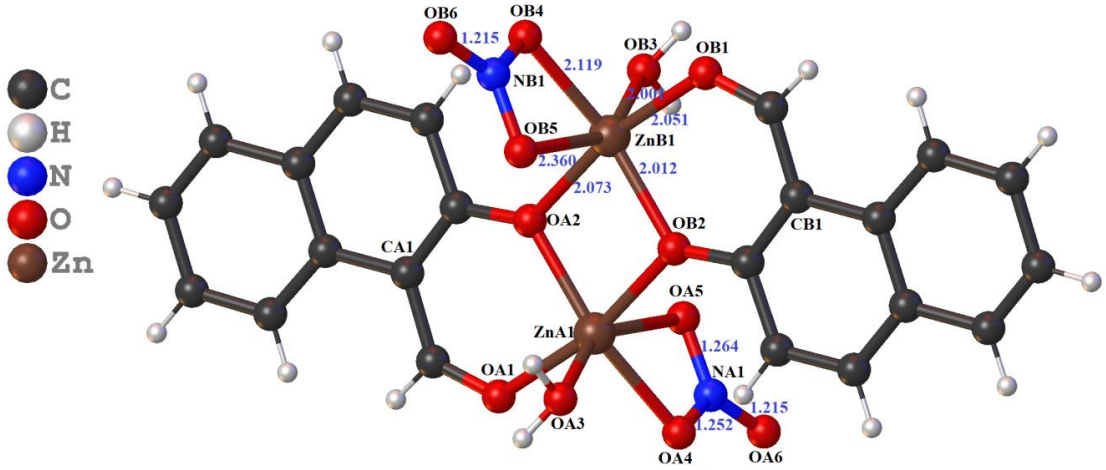


Figure 1. Molecular structure of the [Zn_2*(2-hnaf)*$_2$ (NO_3)$_2$ (H_2O)$_2$] complex

3. Results and discussion

3.1. Structure and bond lengths of obtained complex.

In the obtained complex, the central atom (Zn) has a distorted octahedral structure and is hybridized in the sp^3d^2 state. In the complex compound, *2-hnaf* binds with the central atom as a bidentate ligand, leading to the formation of a six-membered chelate complex. *2-hnaf* is connected to the central atom through oxygen atoms. Bond lengths OA1-ZnA1, OA2-ZnA1 and OA2-ZnB1 (as well as bond lengths OB1-ZnB1, OB2-ZnB1 and OB2-ZnA1) are 2.051, 2.012 and 2.073 Å, respectively. In the complex compound, nitrate anions are also bidentately bonded to the central atom, forming a chelate with a four-membered ring. The bond lengths between the central atom and oxygen atoms in nitrate anions OA4-ZnA1 and OA5-ZnA1 (as well as bond lengths OB4-ZnB1 and OB5-ZnB1) are 2.119 and 2.360 Å, respectively. The reason for the different bond lengths is that one is connected by an ionic bond, while the other is connected by a donor-acceptor bond. Based on ligand field theory, to saturate the primary and additional valencies of the central atom, one water molecule is also coordinated as a monodentate ligand. The bond length of OA3-ZnA1 is 2.001 Å and the oxygen atom in the water molecule is connected to the central atom by a donor-acceptor bond.

In the crystal lattice of the complex compound, molecules are interconnected by strong intermolecular hydrogen bonds (OH...O). Additionally, the stability of the crystal is enhanced due to the face-to-face **π-π** interactions between the naphthalene rings (Figure 2).

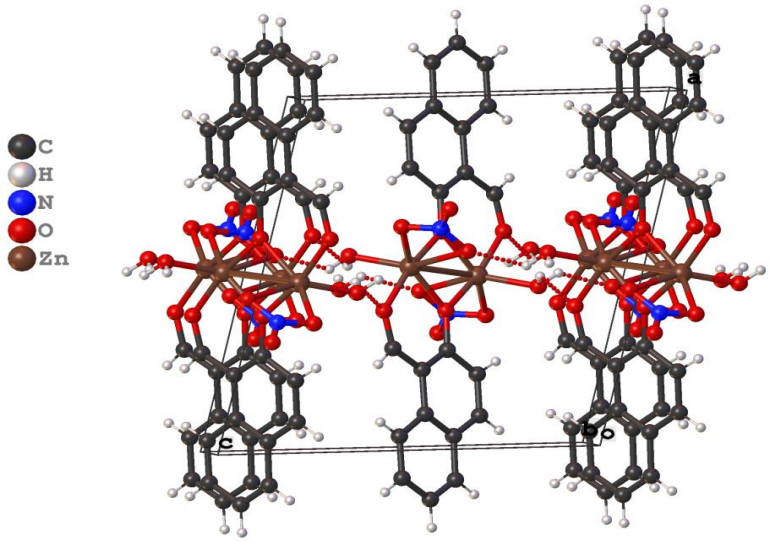


Figure 2. Crystal structure of the complex [Zn_2(*2-hnaf*)$_2$ (NO_3)$_2$ (H_2O)$_2$] (hydrogen bonds are represented by dotted lines)

3.2. Hirshfeld surface of the complex

The Hirshfeld surface analysis of the new complex compound, obtained based on X-ray diffraction data, was carried out using Crystal Explorer 17.5 software (Turner *et al*., 2017). The Hirshfeld surface analysis according to d_{norm} showed a volume of 589.64 Å3, surface area of 482.45 Å2 and dimensions ranging from -0.6386 (red) to 1.3904 a.u. (blue). The external (d_e) and internal (d_i) distances to the nearest nucleus were determined. On the Hirshfeld surface, points with low interaction contribution are indicated in blue, while points with high interaction contribution are shown in red (Figure 3).

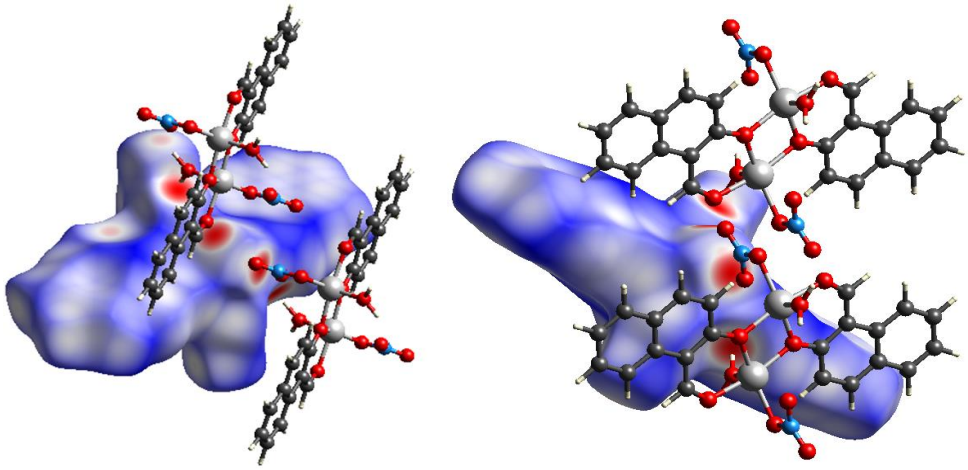


Figure 3. Strong interactions on the Hirshfeld surface of the complex [Zn_2(*2-hnaf*)$_2$ (NO_3)$_2$ (H_2O)$_2$]

Analysis of the two-dimensional fingerprint region plots revealed that H...O/O...H, H...H, and H...C/C...H interactions contribute the most to the Hirshfeld surface. In the complex compound, H...O/O...H interactions account for 35.8%, H...H for 24.3%, and

H...C/C...H for 23.3%, which is expected for molecules dominated by oxygen atoms (Figure 4).

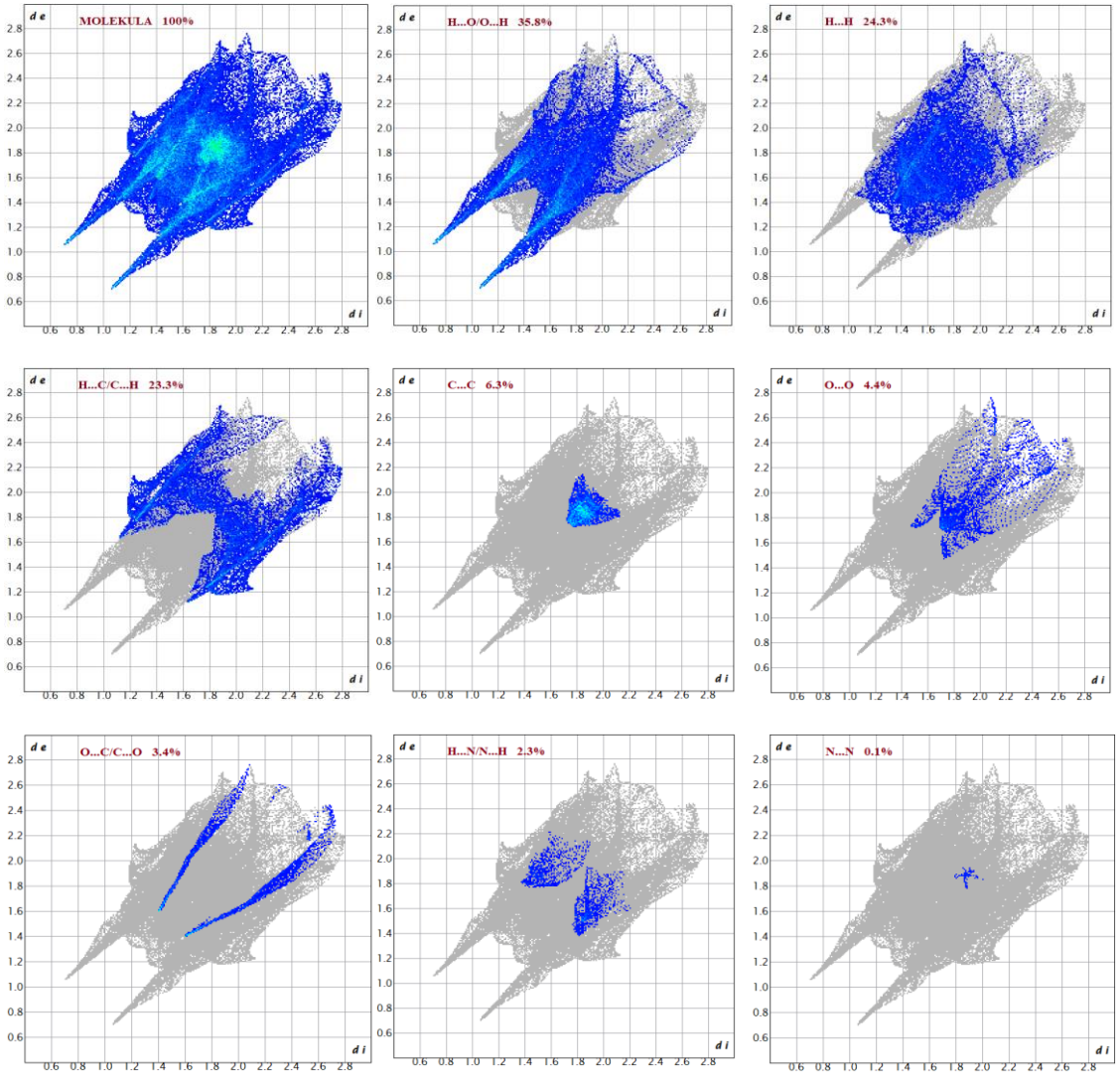


Figure 4. Two-dimensional fingerprint area mapped according to dnorm, representing intermolecular interactions in the crystal of the $[Zn_2(2\text{-}hnaf)_2(NO_3)_2(H_2O)_2]$ complex

In the $[Zn_2(2\text{-}hnaf)_2(NO_3)_2(H_2O)_2]$ complex, among the remaining interactions, C...C (6.3%), O...O (4.4%), O...C/C...O (3.4%) and H...N/N...H (2.3%) interactions are also significant, while the contributions of N...N (0.1%) and N...O/O...N (0.1%) interactions are less significant. The two-dimensional fingerprint area mapped according *to* $d_{norm,}$ representing these interactions, is shown in Figure 4 and the diagram illustrating the contribution of interactions is presented in Figure 5.

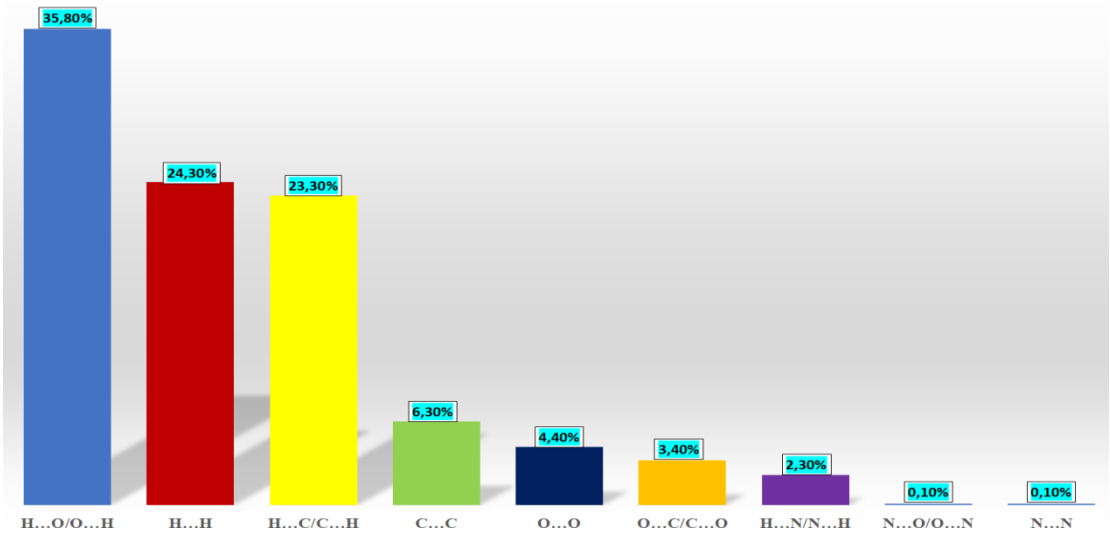


Figure 5. Hirshfeld fingerprint diagram of the [Zn_2*(2-hnaf)*$_2$ (NO_3)$_2$ (H_2O)$_2$] complex

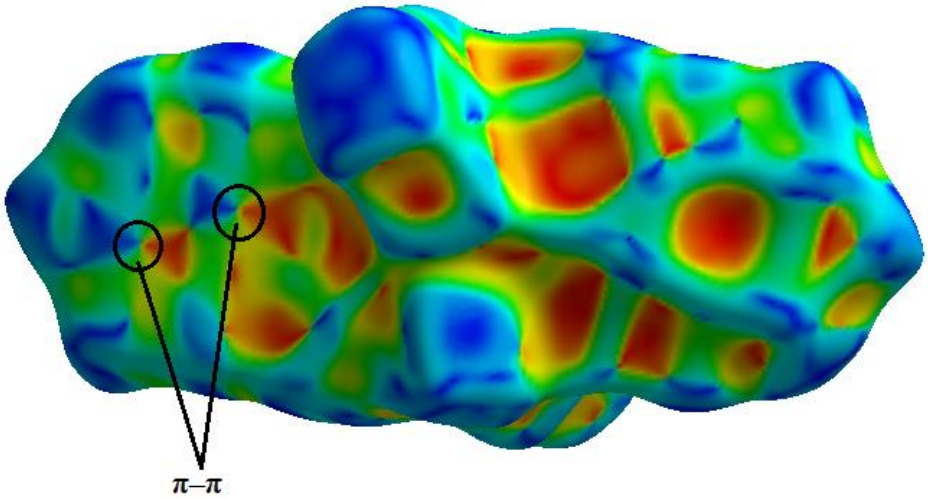


Figure 6. π–π face-to-face interactions on the three-dimensional Hirshfeld surface mapped according to the Shape Index in the [Zn_2*(2-hnaf)*$_2$ (NO_3)$_2$ (H_2O)$_2$] complex

If there is an aromatic ring in the molecule of a complex compound, a π–π face-to-face interaction of the rings is observed. These π–π face-to-face interactions increase the stability of the crystal system (Figure 6). The presence of π–π face-to-face interactions between aromatic rings in the molecule was determined by X-ray diffraction and in the Platon program, it was proven that the distance between the intersections is 3.864 (2) Å (Rasulov *et al.*, 2024). In these studies, complex compounds of organic ligands with colored metal ions were mainly studied. However, the authors (Eshkurbonov & Safarova, 2024) also synthesized polymeric ligands containing functional groups and selective for precious metal ions and due to their macromolecular structure, the possibility of conducting the above research work is limited.

4. Conclusion

As a result of the conducted research, *2-hnaf's* complex compound with zinc nitrate trihydrate was synthesized. The optimal conditions for synthesis were demonstrated. The

composition, molecular and crystal structures of the new complex compound were determined using X-ray diffraction.

It was determined that the central atom in the complex is hybridized in the sp^3d^2 state and has a distorted octahedral structure. It was found that the analyzed metal complexes in the crystal cell cause an increase in the strength of the crystal due to strong intermolecular hydrogen bonds and π-π face-to-face interactions in the aromatic part of the quinoline ring.

Analysis of two-dimensional fingerprint region diagrams obtained using the functions de and di, which indicate the presence of intermolecular π-π interactions and the contribution of individual interactions to the formation of crystal packing, as well as Hirshfeld surface analysis, revealed that H...O/O...H (35.8%), H...H (24.3%) and H...C/C...H (23.3%) interactions contribute the most to the Hirshfeld surface area.

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