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DETERMINATION OF INTERMOLECULAR INTERACTIONS OF NICOTINAMIDE COMPLEXES OF Ni(II) AND Zn(II) 4-FLOROBENZOATES BY HIRSHFELD SURFACE ANALYSIS

Mustafa Sertçelik, Hacali Necefoğlu

Kafkas University, Kars, Türkiye

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Hirshfeld Surface Analysis has been widely used in recent years to investigate intermolecular interactions. Fingerprint graphs allow for the quantitative analysis of intermolecular interaction types. In this study, Hirshfeld surface analyzes of complexes *trans*-Diaquabis(4-fluorobenzoato-*κO*)bis(nicotinamide-*κN*^{1})nickel(II) (Complex **I**) and Bis(4-fluorobenzoato-*κ*^{2}*O,O'*)bis(nicotinamide-*κN*^{1})zinc(II) monohydrate (Complex **II**) were made with the help of CrystalExplorer 17.5 Program and dnorm maps, shape indices, curvature maps were obtained and intermolecular interaction percentages were determined by two-dimensional fingerprint graphics. The most important intermolecular interaction of all complexes is H ··· H interactions. In addition, the dominant H ··· O / O ··· H interactions in the structure are thought to originate from the O-H ··· O hydrogen bonds found in all crystal structures. The adjacent red-blue triangles seen in the shape index plots support the existence of C-H ··· π and π-π interactions between the benzene and pyridine rings. These interactions have also been determined by the single crystal X-ray diffraction method and contribute significantly to the stability of the crystal packing of the complexes.

Keywords: Hirshfeld surface analysis, 4-Fluorobenzoic acid, Nicotinamide, Nickel, Zinc

INTRODUCTİON

In recent years, theoretical chemistry studies have been widely used to examine the structural, physical and biological properties of compounds. The results obtained from the theoretical studies shed light on the prediction and interpretation of the results that can be obtained from the experimental results, and obtaining the theoretical results is much cheaper and faster than the experimental results. For these reasons, it is very important to make theoretical calculations alongside experimental studies in order to avoid wasting money and time for experiments [1,2]. The CrystalExplorer program is also a widely used theoretical calculation program in recent year [3]. Thanks to the Hirshfeld Surface Analysis, it is possible

E-mail address: mustafasertcelik@gmail.com

to determine the Hirshfeld surface, to divide the electron density of the crystal into molecular parts and to define the area where the molecule is located. In this way, structural similarities and differences between the crystal structures studied can be detected. With this analysis, it is possible to identify not only the contribution of intermolecular interactions to crystal packing, but also the properties of different intermolecular interactions [2]. In this study, the intermolecular interactions of the previously synthesized Ni(II) and Zn(II) 4-fluorobenzoates with nicotinamide ligand complexes were investigated by Hirshfeld surface analysis.

MATERIAL AND METHOD

In this study, Hirshfeld surface analysis [4,5] was performed with the CrystalExplorer 17.5 program [3] for a visual representation of the intermolecular interactions of the *trans*-diaquabis(4-fluorobenzoato-*κO*)bis-(nicotinamide-*κN*^{1})nickel(II) (Compleks **I**) [6] and bis(4-fluorobenzoato-*κ*^{2}*O,O'*)bis-(nicotinamide-*κN*^{1})zinc(II) monohydrate (Compleks **II**) [7] complexes (Fig. 1), whose crystal structure had been characterized before. Hirshfeld surface, dnorm and curvature maps and shape index and 2D fingerprint graphs were obtained using the crystallographic information file (CIF) of compounds [3, 4, 8].

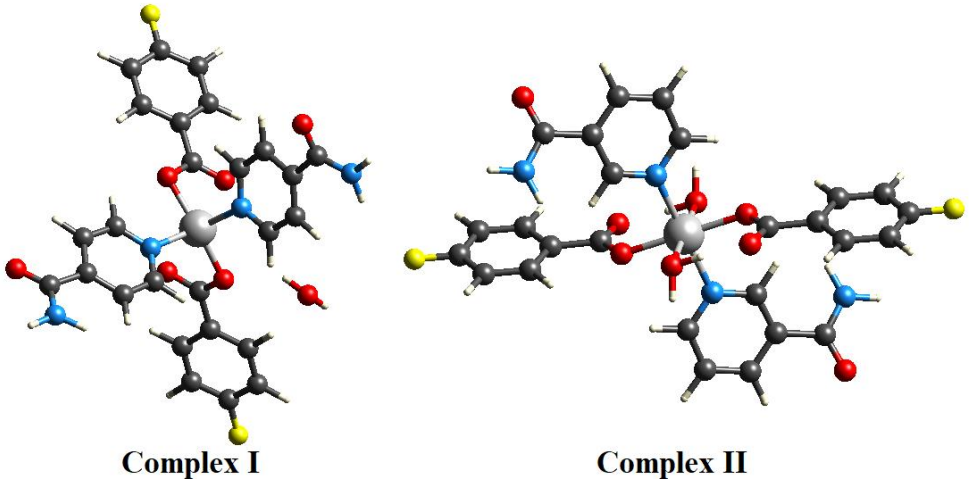

Figure 1. Crystal structures of complexes

FİNDİNGS AND DİSCUSSİON

With Hirshfeld surface analysis, visual graphics are obtained by presenting intermolecular interactions and short or long contacts with different colors and color intensity. In the dnorm maps of the complexes (Figure 2-3), the red and blue surfaces represent distances shorter (closer contact) or longer (different contact) than the Van der Waals radius, respectively. Also, the white surfaces show the distance equal to the sum of the Van der Waals radii. It is seen that especially long distances, that is, different contacts, are more dominant in the dnorm maps of the complexes. In the dnorm map of the complexes, three-dimensional Hirshfeld surfaces were determined in the range of -0.6219 - 1.2880 a.u (Complex **I**) and -0.6686 - 1.8155 a.u (Complex **II**) [9].

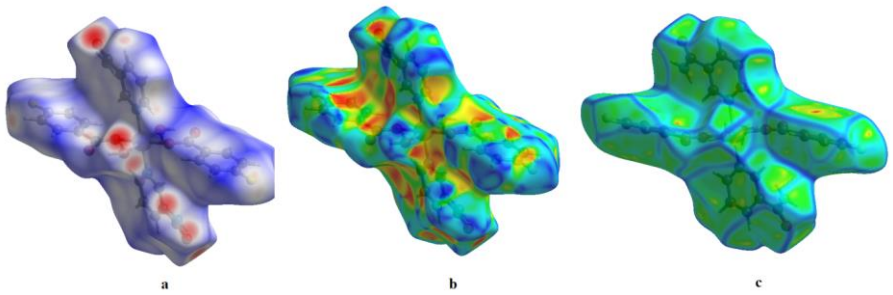

Figure 2. Dnorm map, shape index and curvature map of Complex **I**

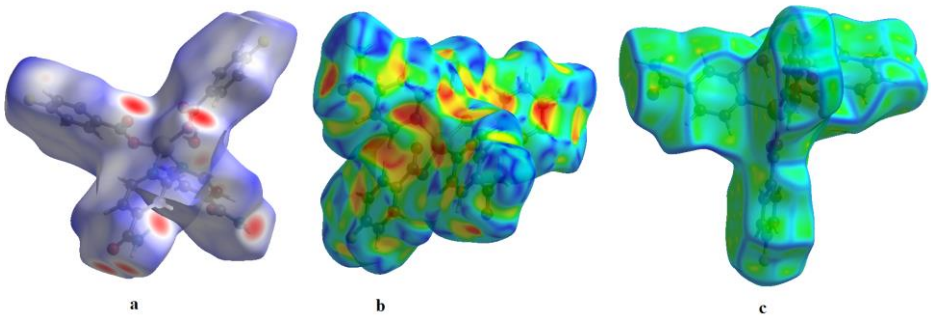

Figure 3. Dnorm map, shape index and curvature map of Complex **II**

When the shape indices of the complexes are examined (Figure 2-3), adjacent red and blue triangles stand out. These confirm the existence of C-H ··· π interactions and π-π stackings between aromatic rings (benzene and pyridine) in the crystal structure of the complexes [9]. According to the 2D fingerprint graphs (Figure 4-5), the most dominant interactions in all complexes are H··· H, H···O/O···H, and H···C/C···H. All interaction percentages are given in Table 1. Due to the abundance of hydrogen on the molecular surface, H ··· H interactions are the most important interactions in all molecules, and the interaction percentages are 32.7% and 32.4% for complexes I and II, respectively. The second most important contribution for Complexes **I** and **II** appears to be O···H/H···O (23.4% and 24.4%, respectively). Also, some minor interactions, F···F, O···F/F···O, and O···N/N···O, that do take place in complex **II**, although not in complex **I**, are given in Table 1.

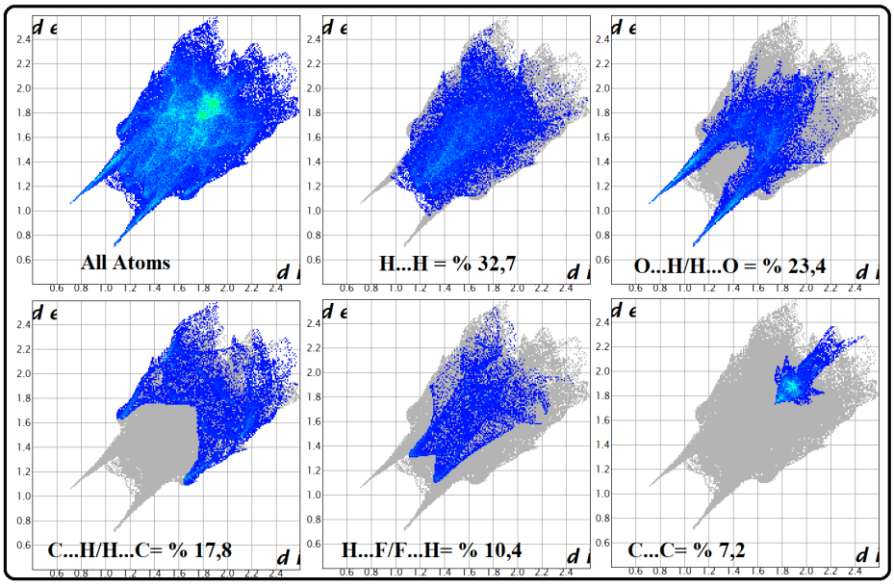

Figure 4. Two-dimensional fingerprint graphs of Complex I

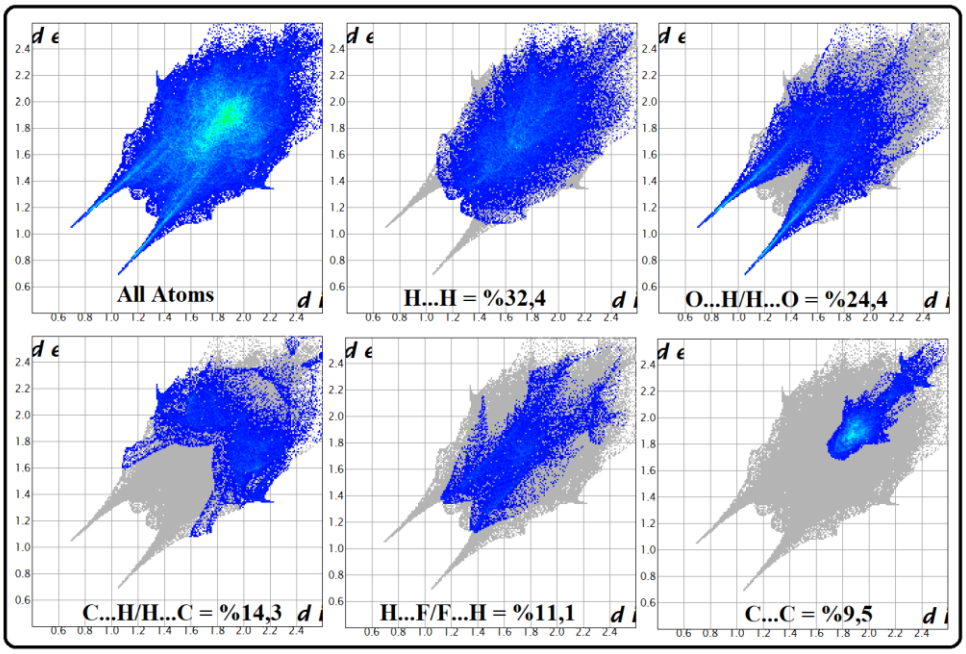

Figure 5. Two-dimensional fingerprint graphs of Complex **II**

Table 1. Molecular interaction percentages of Complexes **I** and **II**.

	Interaction Amount (%)	
Interaction Type	**Complex I**	**Complex II**
C···O/O···C	0,6	1,5
H···C/C···H	17,8	14,3
C···N/N···C	0,2	1,6
C···C	7,2	9,5
H···H	32,7	32,4
H···N/N···H	2,8	1,8
H···O/O···H	23,4	24,4
H···F/F···H	10,4	11,1
C···F/F···C	3,0	1,1
F···F	-	1,1
N···F/F···N	0,7	0,4
O···F/F···O	1,1	0,4
N···O/N···O	-	0,2
N···N	-	0,2

CONCLUSİON

In this study, Hirshfeld surfaces and 2D fingerprint graphics of Ni(II) and Zn(II) 4-fluorobenzoat nicotinamide complexes were determined. According to the results of Hirshfeld Surface Analysis, in all structures H...H, H...O/O...H, H...C/C...H, H...F/F...H, C ...C, interactions have been detected. The H...H interactions are the interaction that contributes

the most to the crystal structures. One of the dominant interactions, H...O / O...H interactions, also confirms the existence of hydrogen bonds in the crystal structure. The π-stacking interactions between the benzene and pyridine rings in the structure of the complex are supported by the presence of adjacent red and blue triangles in the shape index. As a result, the results obtained from single crystal X-ray analysis and Hishfeld surface analysis support each other.

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