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Research Article

The Hirshfeld Surface and Fingerprint Plot Analysis of Weak Interactions in The Crystal Structure of Trimeric Complex of Coper(I) Dichloride with Methylene Blue

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Annotation

Crystals of (I) is monoclinic, space group is P21/n, a=15.1327(5), b=14.9456(3), c=16.5175(5) Å, β = 115.236(4)°, Z=4. Complex (I) is built from trimeric molecule [Cu (Mb)Cl2] linked through π–π interactions. The intermolecular short contacts in the trimeric complex [Cu (Mb)Cl2] (I) (where Mb is methylene blue, methylthioninium cation) were studied by the Hirshfeld surface and fingerprint plot analysis. The 2D fingerprint plots confirmed the predominance of H···H (39.5 %) intermolecular interactions and while a small contribution of C···C contacts (8.0 %).

Keywords: copper (I); methylene blue; π-π stacking; Hirschfeld surfaces

Introduction

Methylene blue (MB, methylthioninium chloride), a phenothiazine known for its ability to cross the blood-brain barrier and exert neuroprotective effects, is considered a potential therapy, especially for neurodegenerative diseases [1,2]. Among its beneficial properties, MB is a redox cycle stabilizer and an electron donor [1]. With the discovery of its antioxidant properties, it was proposed as a therapeutic agent in neurodegenerative and psychotic disorders with its features of mitochondrial dysfunction and redox cycle regulation. Methylene blue has been proven to inhibit the accumulation of tau proteins, which is considered among the causes of Alzheimer's disease (AD), treat mitochondrial dysfunction with its regulating effect on the redox cycle, and to inhibit formation of ROS molecules. In given paper, the close contacts involving also π–π intermolecular interactions between MB^+ cations are analyzed by using the Hirshfeld surfaces analysis.

Materials and Methods

The complex (1) was obtained in the result mechanochemical reaction of the copper (II) chloride with [MB]Cl·$5H_2O$ using of DMF as assistant-solvent. During reaction copper (2+) is reduced to copper (1+). Hirshfeld surfaces calculations were performed by using the Crystal Explorer 21 program [3,4].

Results and Discussions

Crystals of (1) is monoclinic, space group is $P2_1/n$, a=15.1327(5), b=14.9456(3), c=16.5175(5) Å, β= 115.236(4)°, Z=4. Molecular and crystal structures are presented in (Figures 1 & 2). The crystal structure of compound (I) is composed of the trimer consisting of the three $CuCl_2$(MB) complexes connected mutually via π···π interactions with the mean interplanar distance 3.376 Å and close centroid-centroid distances between aromatic central rings lie in the range from 3.383 to 3.500 Å. Any type of intra- or intermolecular interactions can be demonstrated in detail by using Hirshfeld surface analysis of the crystal structure. In given paper, the crystal structure of complex (I) was studied by using of the Hirshfeld surface analysis to be visualizing the short contacts between neighboring $(MB)^+$ cations [3]. On the d_{norm} surface, the red spots represent the C-H···Cl and C–H···C weak interactions acting between the middle molecule and two neighboring molecules. The blue colored

area of that surface is the area which is completely free from close contacts (Figure 3). In the shape-index of the complex (I) Figure 4 convex blue regions represent hydrogen donor groups and concave red regions represent hydrogen acceptor groups in the weak interactions. As seen on this Figure, neighboring red and blue triangles confirm the existence of intermolecular interactions resulting from π-π stacking between the aromatic rings in the crystal structures of the complexes. On the 2D fingerprint plots, the blue areas show the groups of atoms involved in the close intermolecular contacts. To the right of each figure is a 2D fingerprint graph for each short contact. The 2D fingerprint plots confirmed the predominance of H···H (39.5 %) Figure 5a intermolecular interactions and while a small contribution of C···C contacts (8.0 %) Figure 5b between neighboring $[MB]^+$ cations.

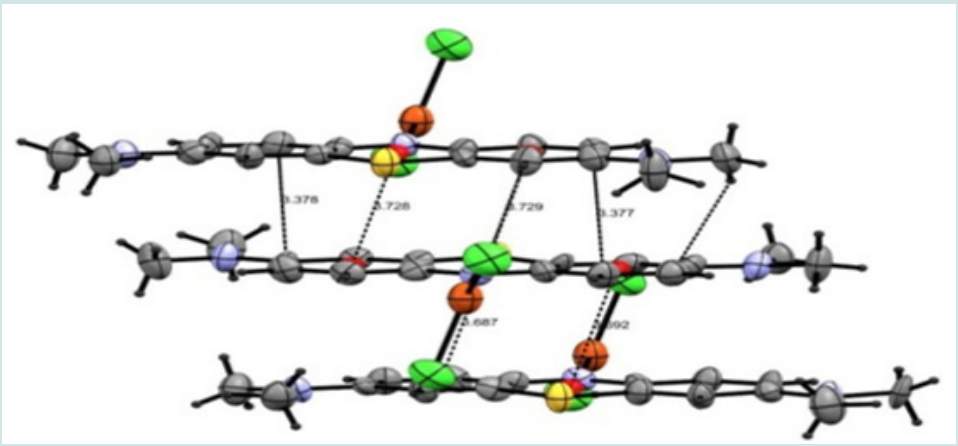

Figure 1: Molecular structure of the complex (I).

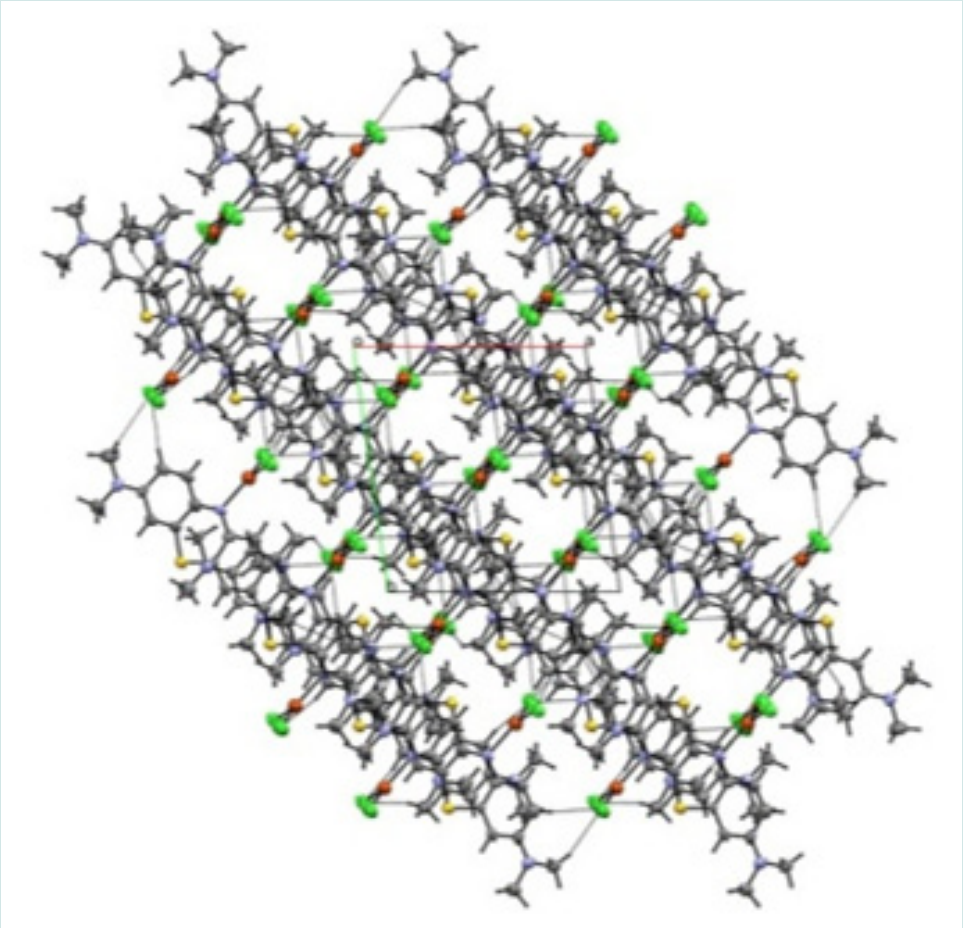

Figure 2: The crystal structure of the complex (I). Dotted lines show close contacts.

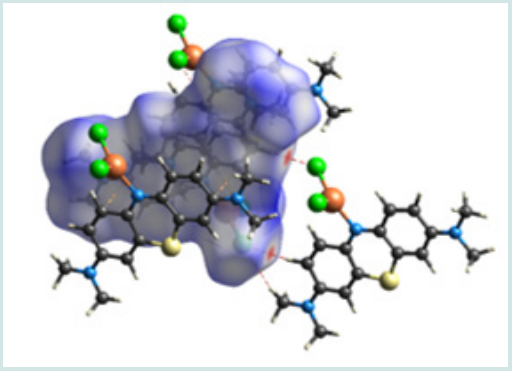

Figure 3: View of the three-dimentional Hirshfeld surface for the [MB]+ anion in the middle of trimer of the title compound plotted over d^{norm}.

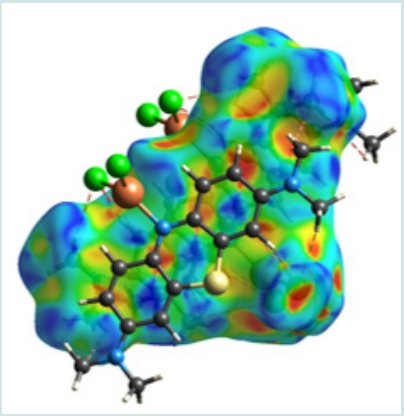

Figure 4: Hirschfeld surface for the middle Mb+ cation of the complex (I) plotted over shape-index

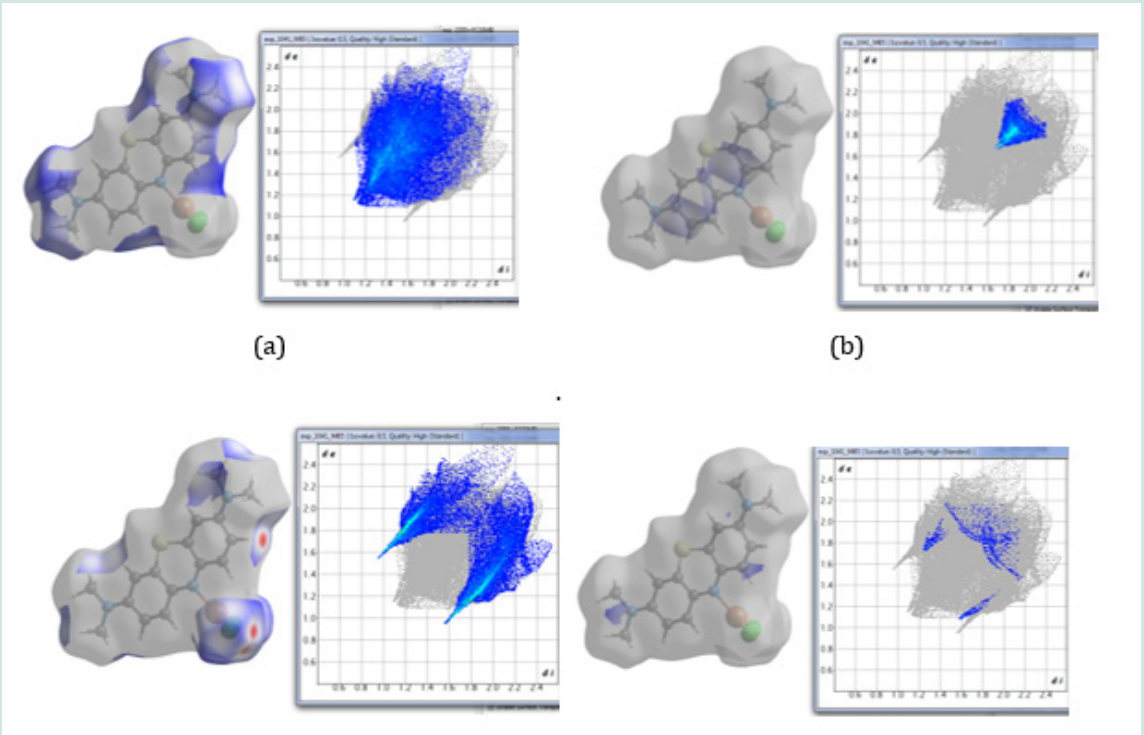

Figure 5: 2D fingerprint plot for H···H (a), C···C (b), Cl…H/H…Cl (a) (29.3 %) and N…H (b) (1.5 %) contacts.

Conclusion

Close contacts in the crystal structure of trimeric complex $[CuCl_2(Mb)]_3$ were studied by using the Hirshfeld surfaces and fingerprint plots analysis. π−π stacking interaction is shown on the shape-index of the complex.

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