HIRSHFELD SURFACE ANALYSIS OF π-π STACKING INTERACTIONS IN THE CRYSTALS OF Cu(II) COMPLEXES WITH AROMATIC LIGANDS

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Intermolecular interactions often play crucial role biochemical processes and in formation of structure and physical properties of molecular solids. Among them the π···π stacking interactions between aromatic ligands coordinated to metal are less studied but are essential for rational design of metal-organic materials with desired architecture. The understanding of contribution of these interactions in overall crystal packing is important for crystal engineering. This work presents the results of the analysis of stacking interactions and their influence on the architecture of seven crystal structures of mono- and binuclear copper(II) complexes with composition $[Cu(acac)(phen)(dmf)]BF_4$ (**1**), $[Cu(acac)(phen)H_2O]BF_4$ (**2**), $Cu(acac)(phen)Cl]MeOH$ (**3**), $[Cu_2(acac)_2(phen)_2(4,4'\text{-bpy})](BF_4)_2$ (**4**), $[Cu_2(acac)_2(2,2'\text{-bpy})_2(4,4'\text{-bpy})](BF_4)_2$ (**5**), $[Cu_2(acac)_2(2,2'\text{-bpy})_2(bpe)](BF_4)_2(H_2O)_2$ (**6**) and $[Cu(acac)(2,2'\text{-bpy})(H_2O)][Cu(acac)(2,2'\text{-bpy})](BF_4)_2$ (**7**) [1], (*acac*=acetylacetonate, *phen*=phenanthroline, *bpy*= bipyridine, and *bpe*=1,2-bis(4-pyridyl)ethane).

We have used the Hirshfeld surfaces and intermolecular energy analyses for study of such interactions. The Hirshfeld surfaces were plotted in the range 0.4-2.4 Å for each of and d_i and d_e. The analysis of 2D fingerprint plots show that a major HS contribution of 13.6-21.8% and 36,4-48.6% comes from two types of contacts, namely C···H and H···H, respectively. The contribution of C···C interactions largely correspond to *π-π stacking* interactions, which contribute to 1.9 - 6.2% of the Hirshfeld surfaces and appear on the fingerprint plots as a single triangle at about $d_e = d_i \approx 1{,}7$ Å (Figure 1 and 2). These interactions dominate in the packing of the structure of mentioned compounds.

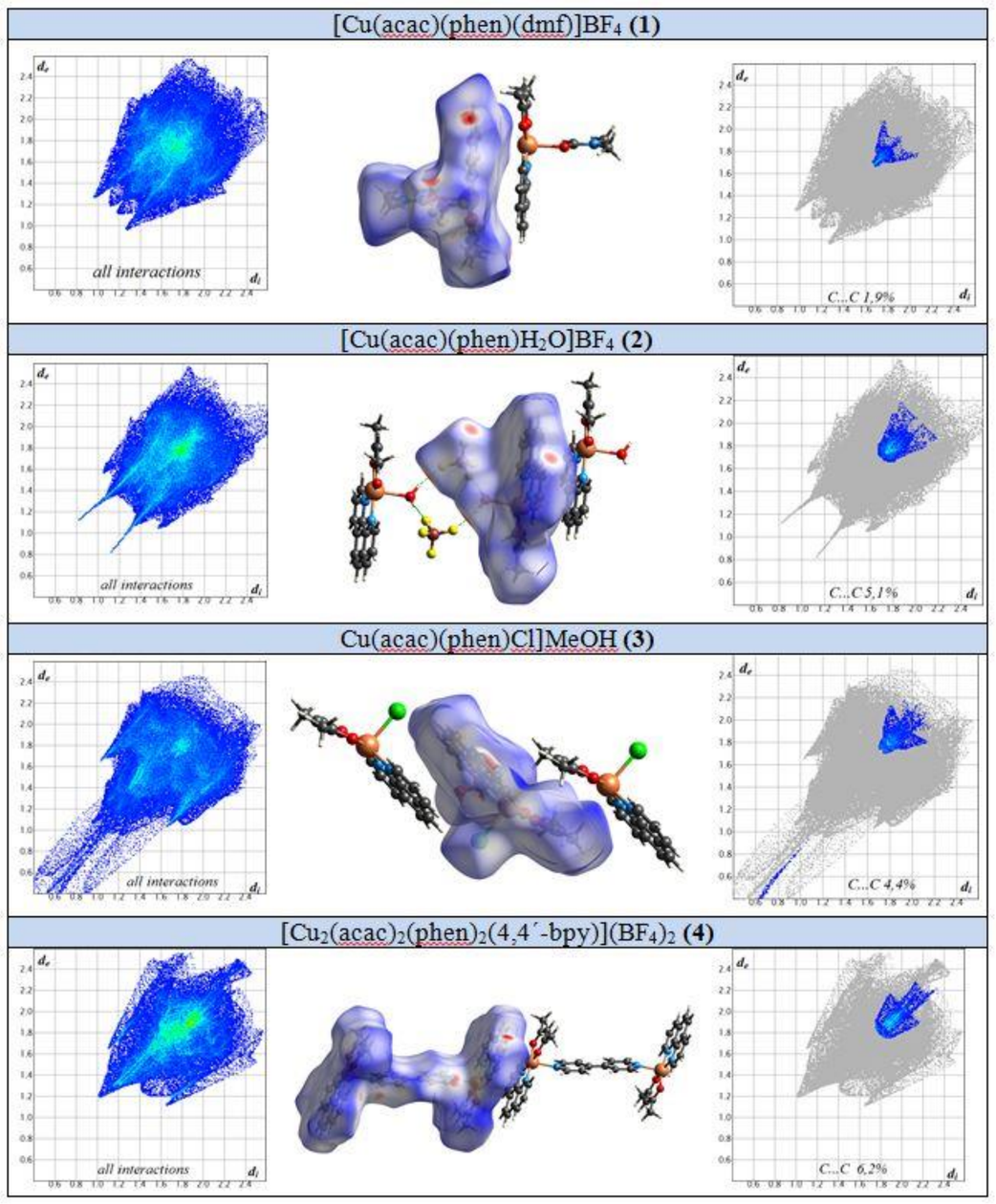

Fig.1. The Hirshfeld surfaces and 2D fingerprint plots for the strucures **1-4**

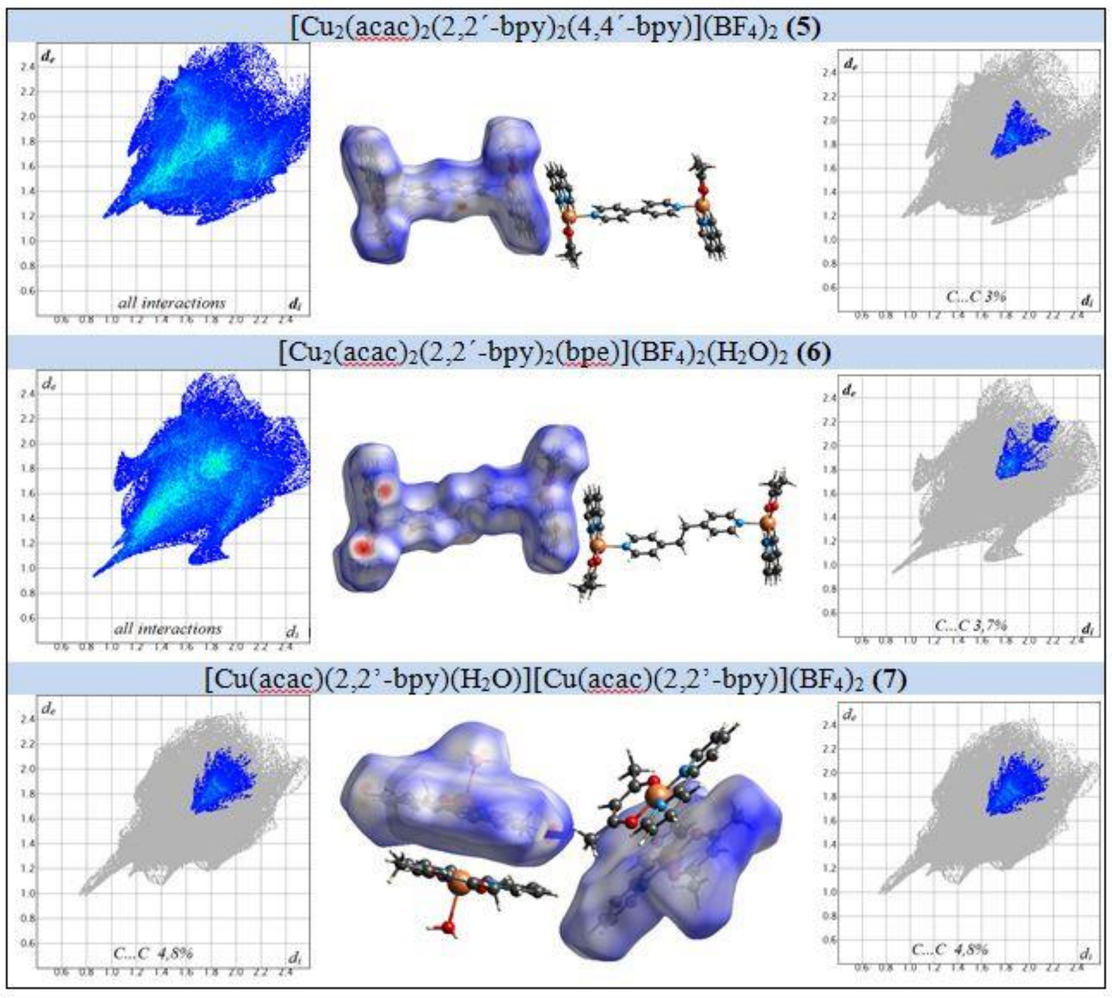

Fig. 2. The Hirshfeld surfaces and 2D fingerprint plots for the strucures **5-7**

The intermolecular energy analysis calculated according to the energy model CE-B3LYP with 6-311G (d,p) basis set has revealed that the energy of π-π stacking interactions between the fragments involving metal chelate and the ligands fall in the range -41.1 — -80.9 kJ / mol and confirmed a significance of such interaction to the stabilization of supramolecular architecture (Figure3).

a)

	N	Symop	R	Electron Density	E_{ele}	E_{pol}	E_{dis}	E_{rep}	E_{tot}
	1	-x, -y, -z	4.51	B3LYP/6-31G(d,p)	-19.6	-8.3	-108.2	65.1	-80.9
	1	-x, -y, -z	7.72	B3LYP/6-31G(d,p)	-10.3	-3.0	-64.7	40.4	-44.5

b)

	N	Symop	R	Electron Density	E_{ele}	E_{pol}	E_{dis}	E_{rep}	E_{tot}
	1	-x, -y, -z	6.53	B3LYP/6-31G(d,p)	-15.8	-2.0	-75.2	39.7	-59.2

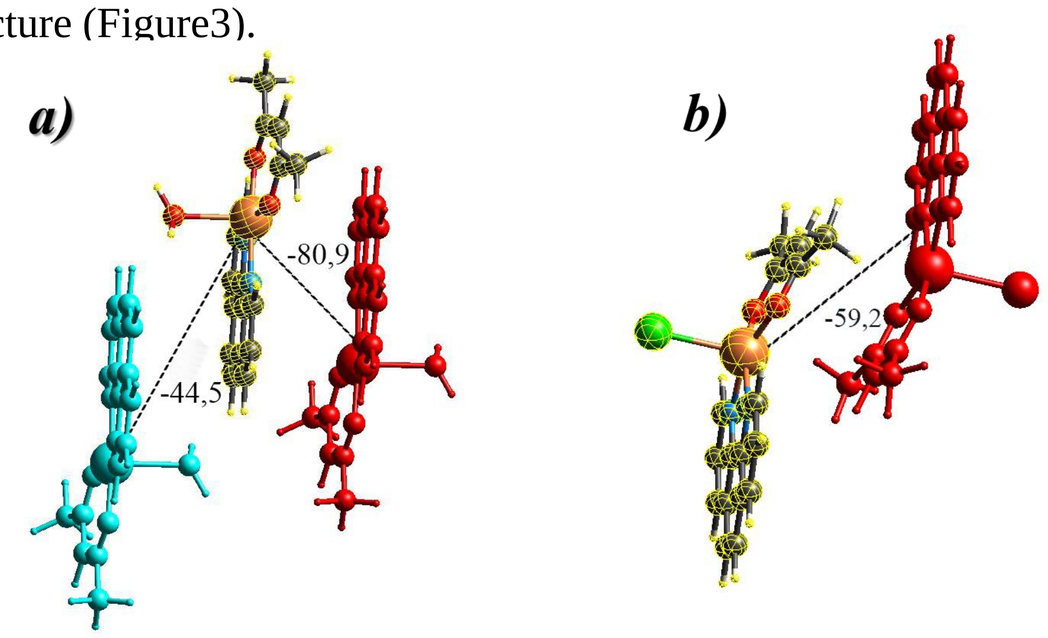

Fig.3. Interaction energy between neighboring molecules in the fragments of crystal packing in **2 (a)** and **3 (b)**

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