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Towards quantitative analysis of the non-covalent interactions in a newly synthesized phenanthroline-based nickel(II) complex : A combined experimental and computational study

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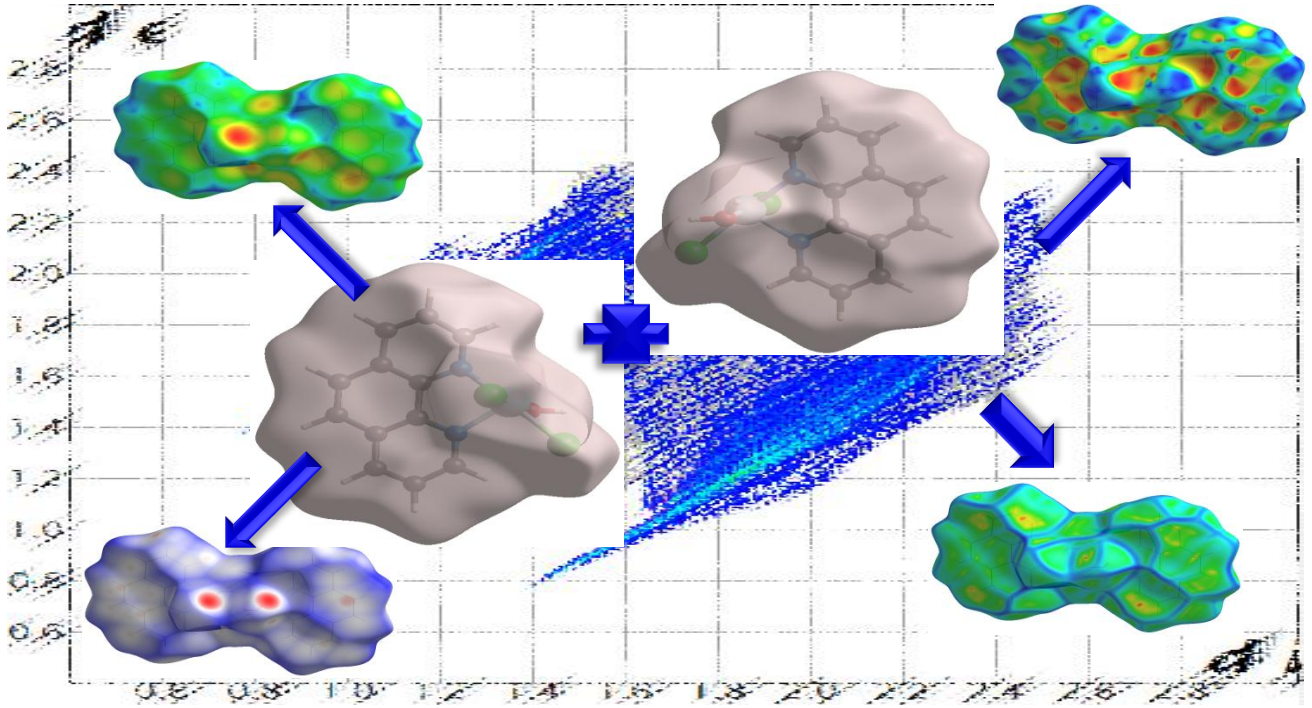
LASPI²A

Towards quantitative analysis of the non-covalent interactions in a newly synthesized phenanthroline-based nickel(II) complex : A combined experimental and computational study

Graphical Abstract



Abstract:
A new phenanthroline-based nickel(ii) complex was synthesized and fully characterized by single-crystal X-ray diffraction. Its crystal structure revealed that it comprises $Ni_2Cl_4(H_2O)_2(Phen)_2$ dimmers linked *via* O–H...Cl hydrogen bonds. In order to get better insights into the hydrogen bonds and the intermolecular interactions holding the molecules together, a Hirshfeld surface analysis was carried out. Besides, the structure of the studied complex was optimized at M06-2X/6-31G(d)(LANL2DZ) level. Furthermore, the molecular orbital energy diagram, the contour plots of the molecular orbitals and the molecular electrostatic potential (MEP) map were calculated and discussed.

Keywords: Ni(II) complex, crystal Structure, hydrogen bonds, non-covalent interactions, *Hirshfeld* surface analysis, MEP map, quantum chemical calculations.

Introduction

Phenantroline derivaties are a very important class of organic and organometallic molecules due to their attractive coordinating features with transition metals [1]. Hence, photochemical properties of phenantroline-based metal complexes were recently reported [2]. Their biological applications were intensively studied [3] and their anticancer properties proved [4]. Additionaly, this class of coordination complexes are found to be interesting as potentiometric sensors [5] and are able to interact with DNA in an intercalative fashion inducing in some cases the DNA cleavage [6]. İn order to contribute to the better understanding of these materials, we report herein the structural and the electronic properties of a newly synthesized phenantroline-based Ni(II) complex [7]. İts non-covalent interactions will be fully analyzed by means of the *Hirshfeld* surface analysis [8,9], its molecular orbital energy diagram (MOED) and molecular electrostatic potential (MEP) map will be examined.

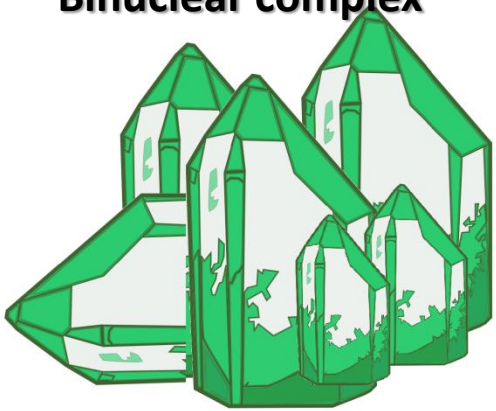
Results and discussion

Synthesis

$C_{12}H_8N_2 \cdot HCl \cdot H_2O$ + $(NiCl_2.6H_2O + H_2O)$ + $H_3PO_3 + H_2O)$

1,10-Phenanthroline hydrochloride monohydrate

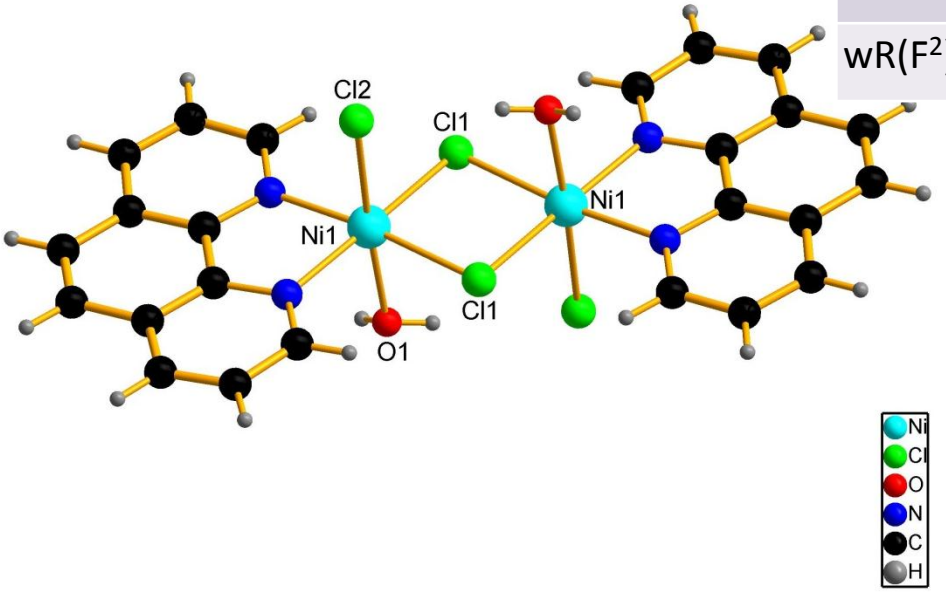
$Ni_2Cl_4(H_2O)_2(Phen)_2$
Binuclear complex



Results and discussion

Crystal structure

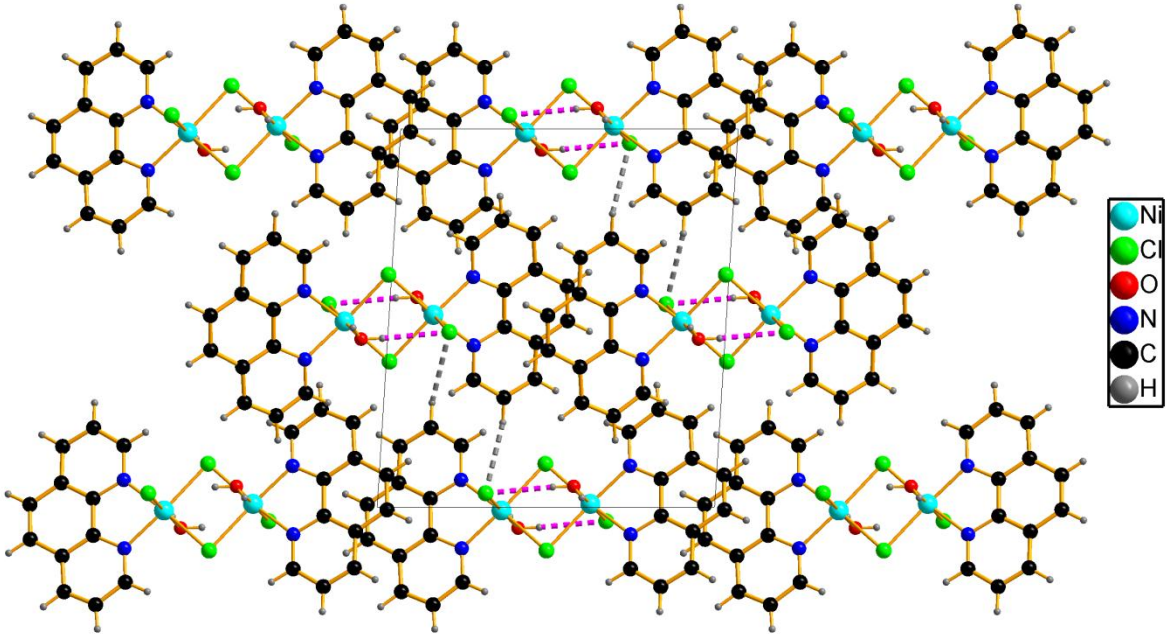
Space Group	$P2_1/n$
a (Å)	12.6640 (5)
b (Å)	6.8322 (3)
c (Å)	14.2054 (5)
β (°)	93.569 (9)
$R[F^2 > 2\sigma(F^2)]$	0.031
$wR(F^2)$	0.082



Results and discussion

Hydrogen bonding

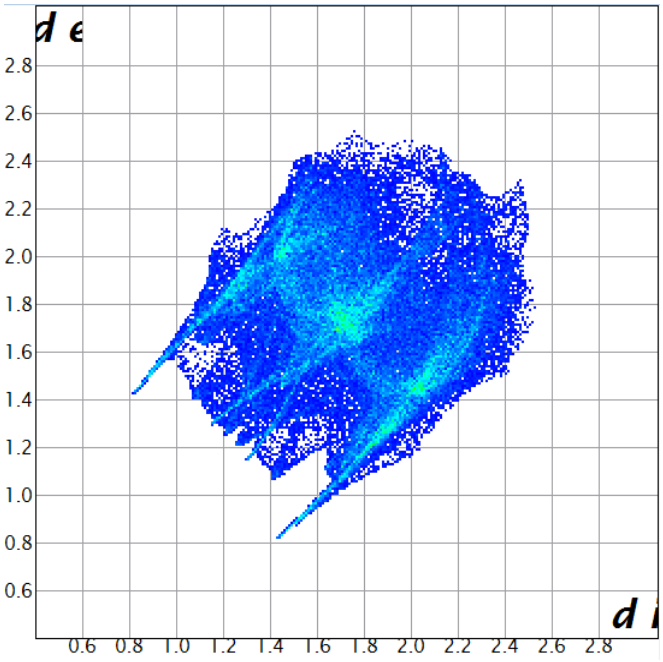
D—H···A	D—H	H···A	D···A	D—H···A
O1—H1o1···Cl2^{i}	0.78 (3)	2.41 (3)	3.1821 (17)	168 (3)
Symmetry code: (i) x, y−1, z.				



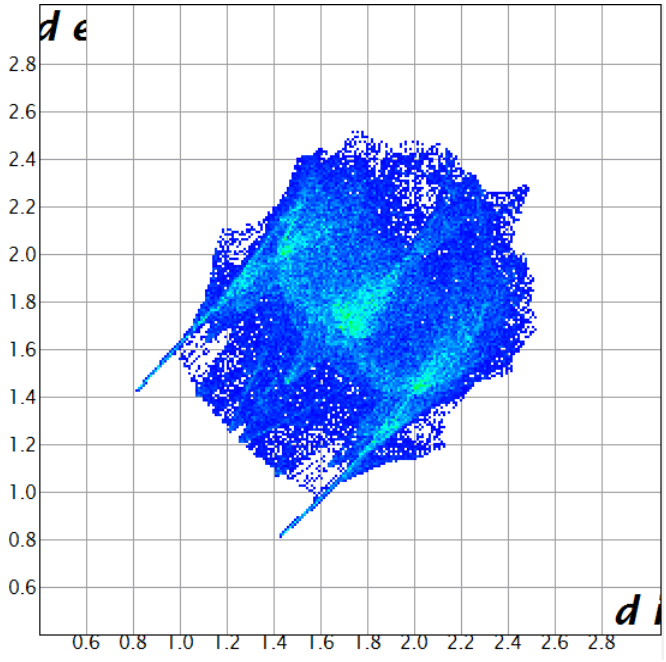
Results and discussion

Hirshfeld surface analysis

All contacts :



Asymmetric unit

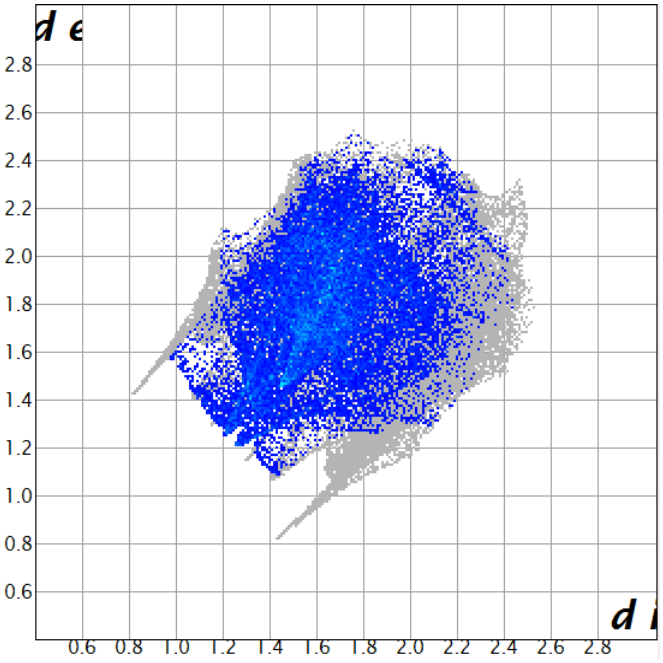


Binuclear complex

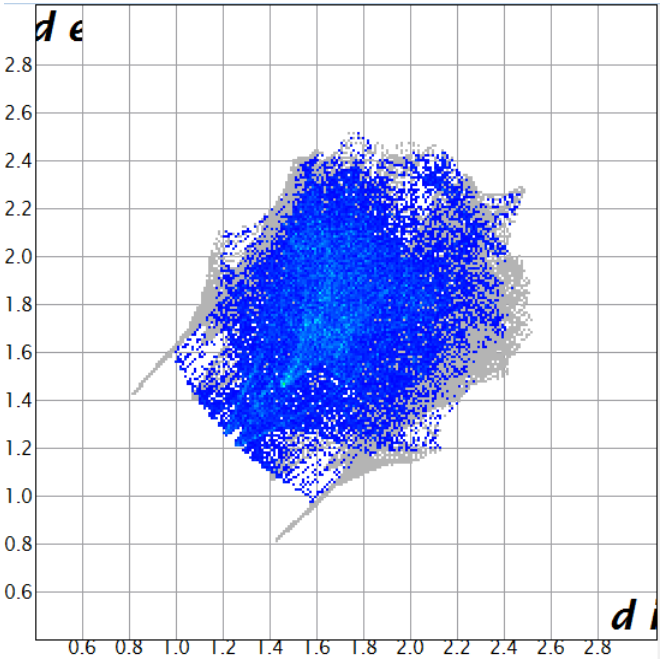
Results and discussion

Hirshfeld surface analysis

H…H contacts :



Asymmetric unit
(30.1%)



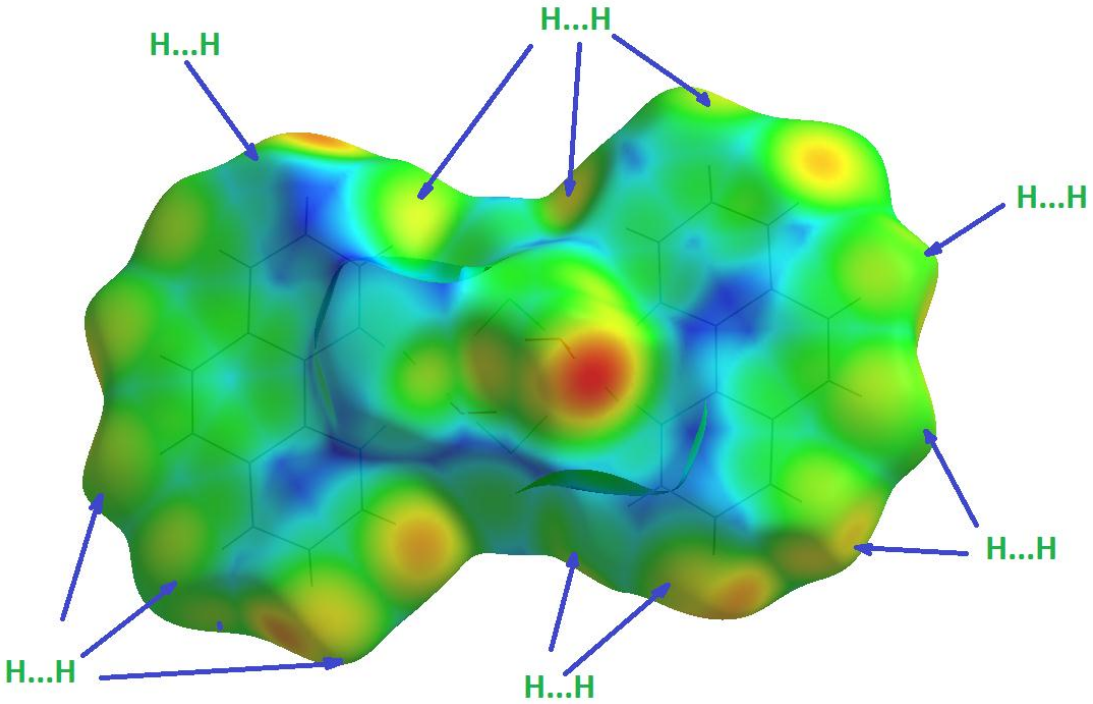
Binuclear complex
(35.6%)

Results and discussion

***Hirshfeld* surface analysis**

H…H contacts :

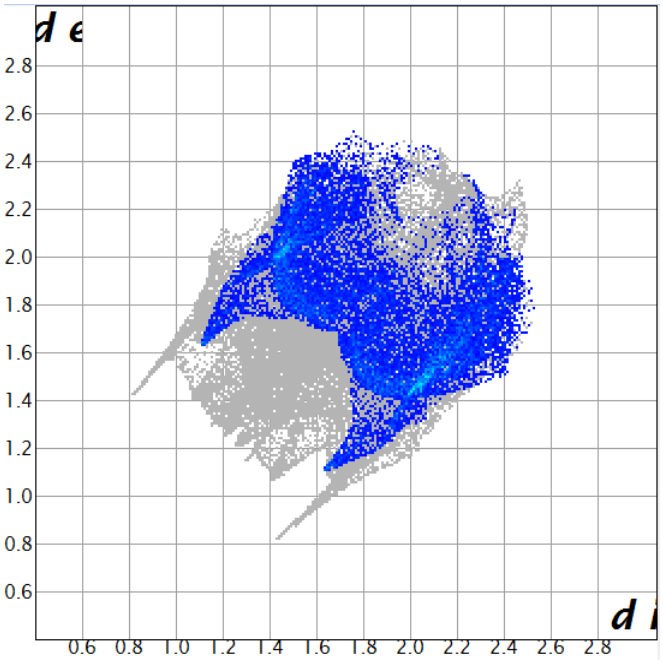
d_i Representation



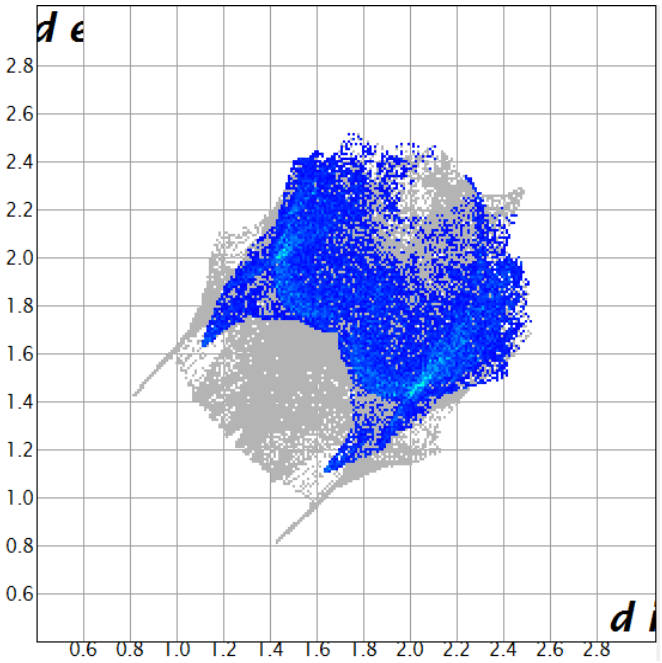
Results and discussion

Hirshfeld surface analysis

C…H/H…C contacts :



Asymmetric unit (23.0%)

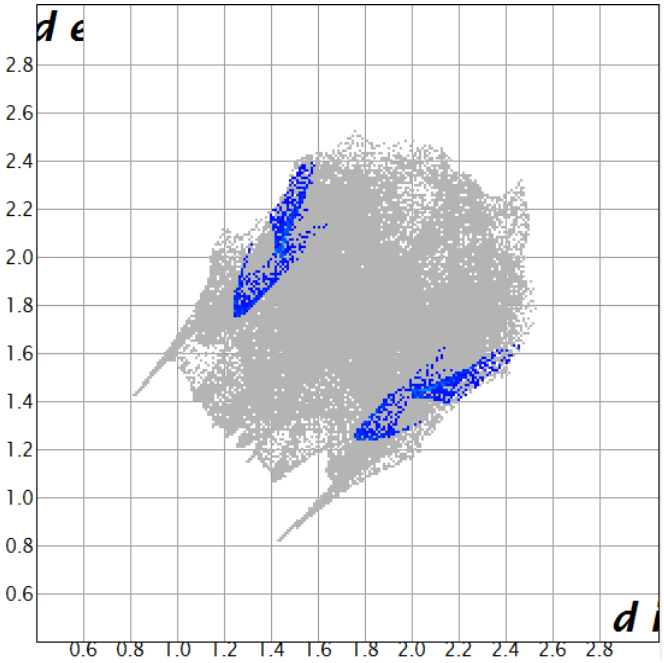


Binuclear complex (26.3%)

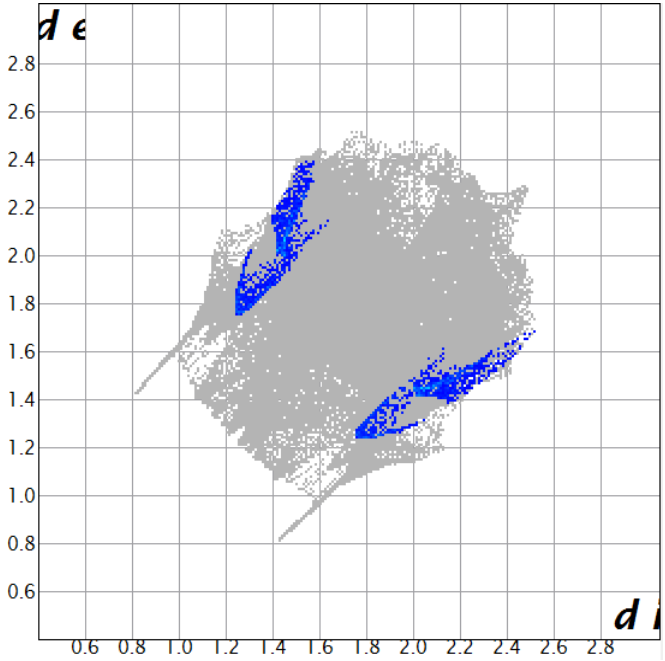
Results and discussion

Hirshfeld surface analysis

N…H/H…N contacts :



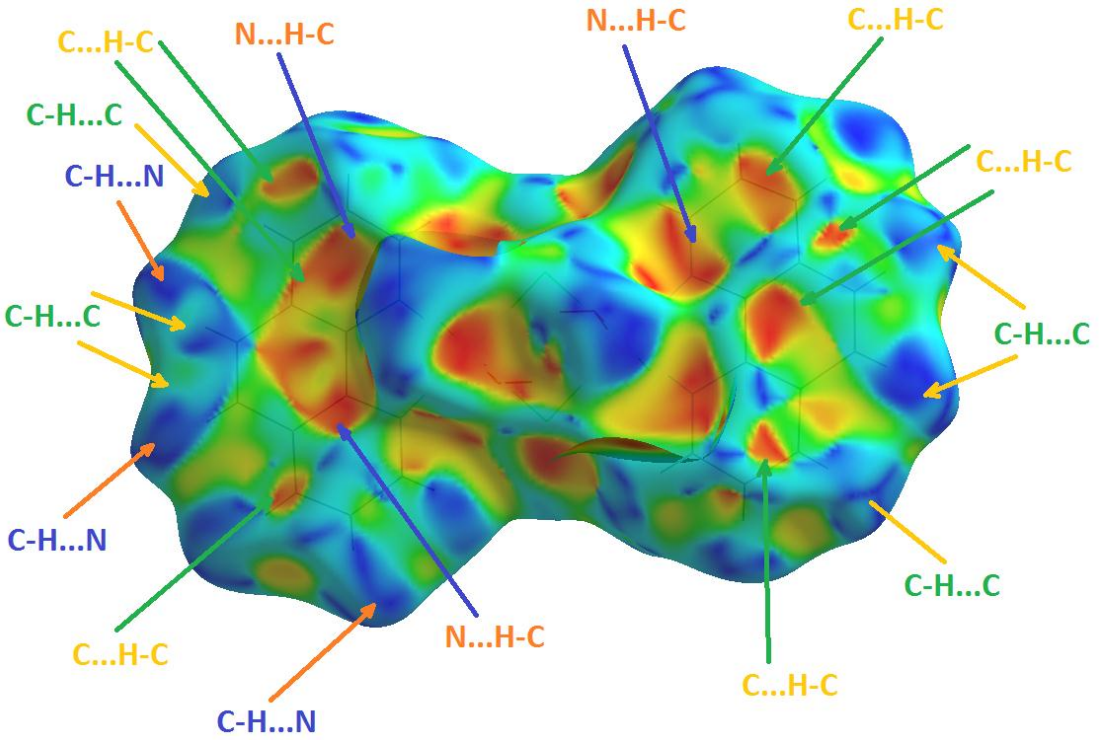
Asymmetric unit
(2.4%)



Binuclear complex
(2.7%)

Results and discussion

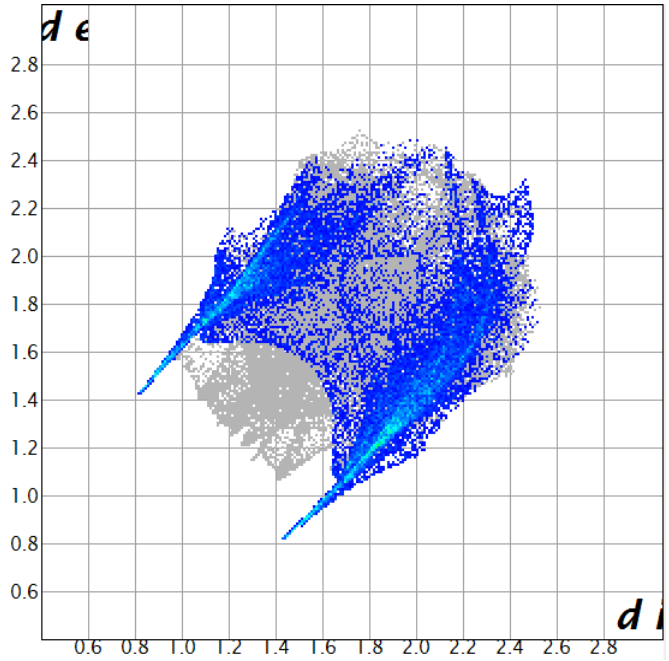
***Hirshfeld* surface analysis**
N…H/H…N and C…H/H…C contacts :
***Shape index* Representation**



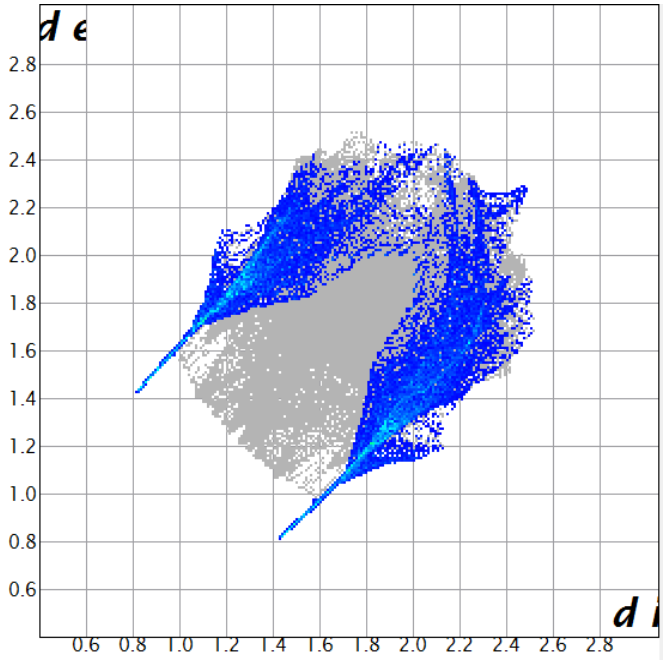
Results and discussion

Hirshfeld surface analysis

Cl…H/H…Cl contacts :



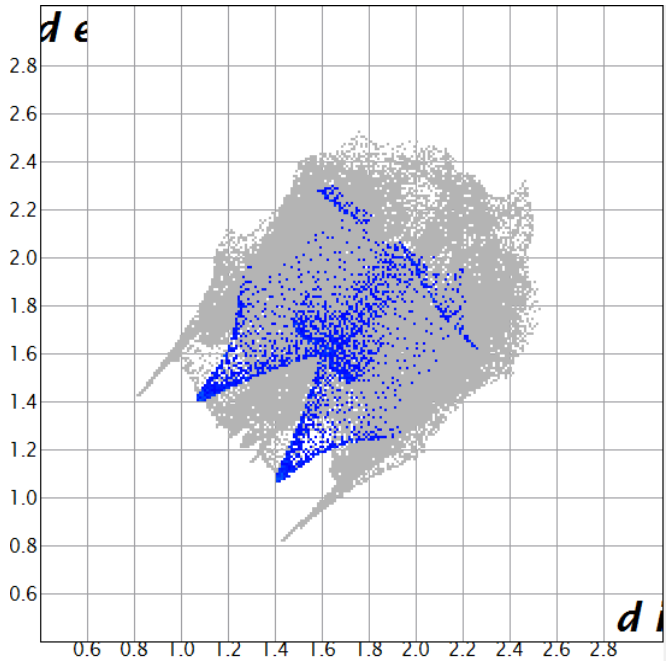
Asymmetric unit (30.4%)



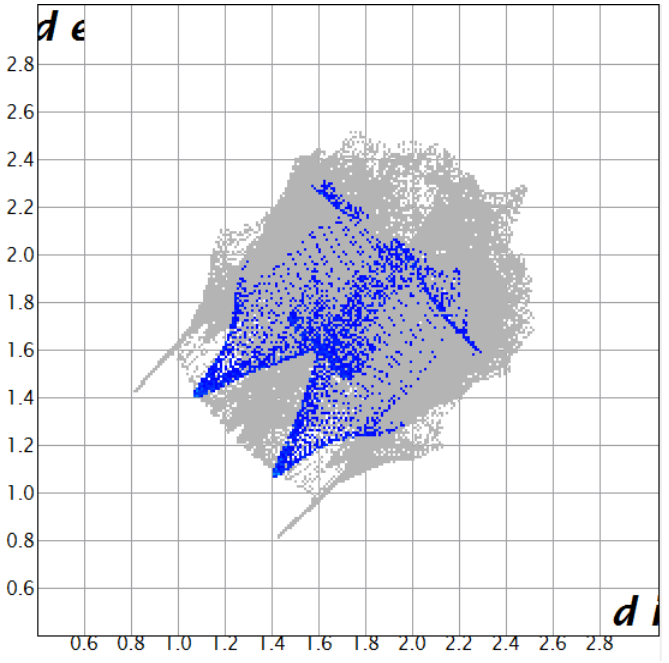
Binuclear complex (23.4%)

Results and discussion

Hirshfeld surface analysis
O…H/H…O contacts :



Asymmetric unit
(3.0%)

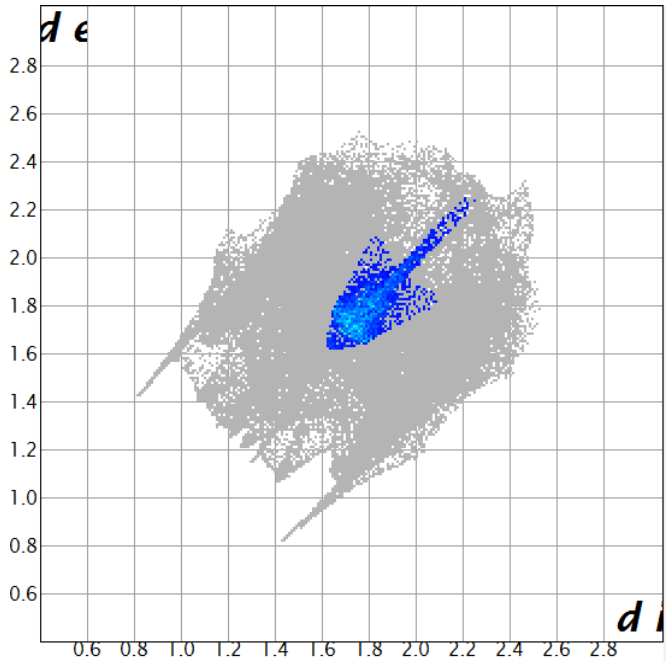


Binuclear complex
(3.5%)

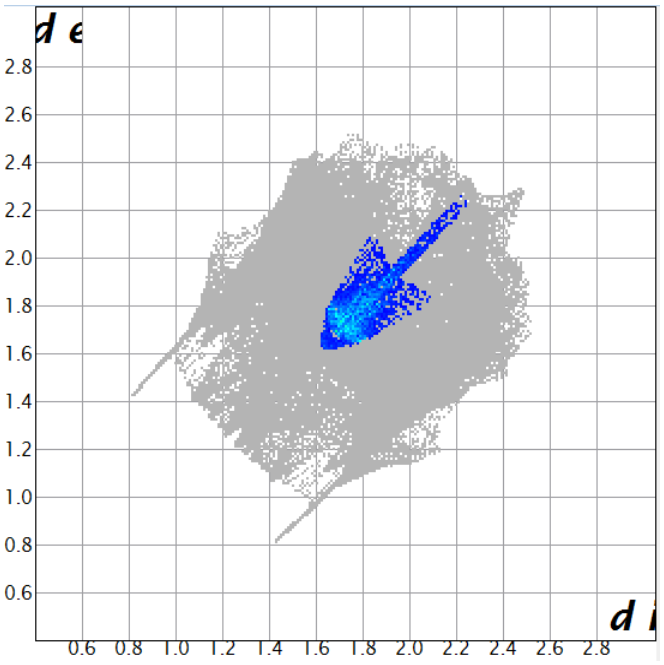
Results and discussion

Hirshfeld surface analysis

C…C contacts :



Asymmetric unit
(5.8%)



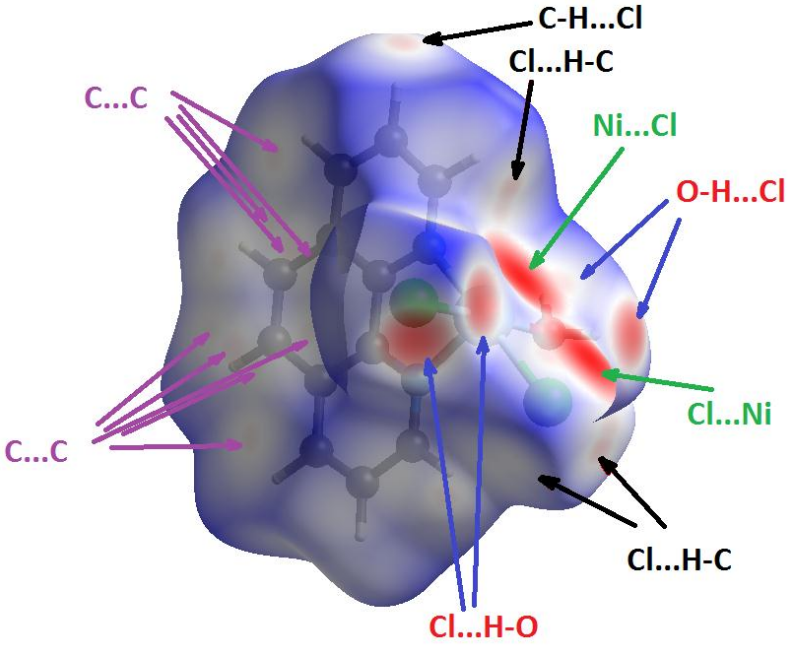
Binuclear complex
(6.6%)

Results and discussion

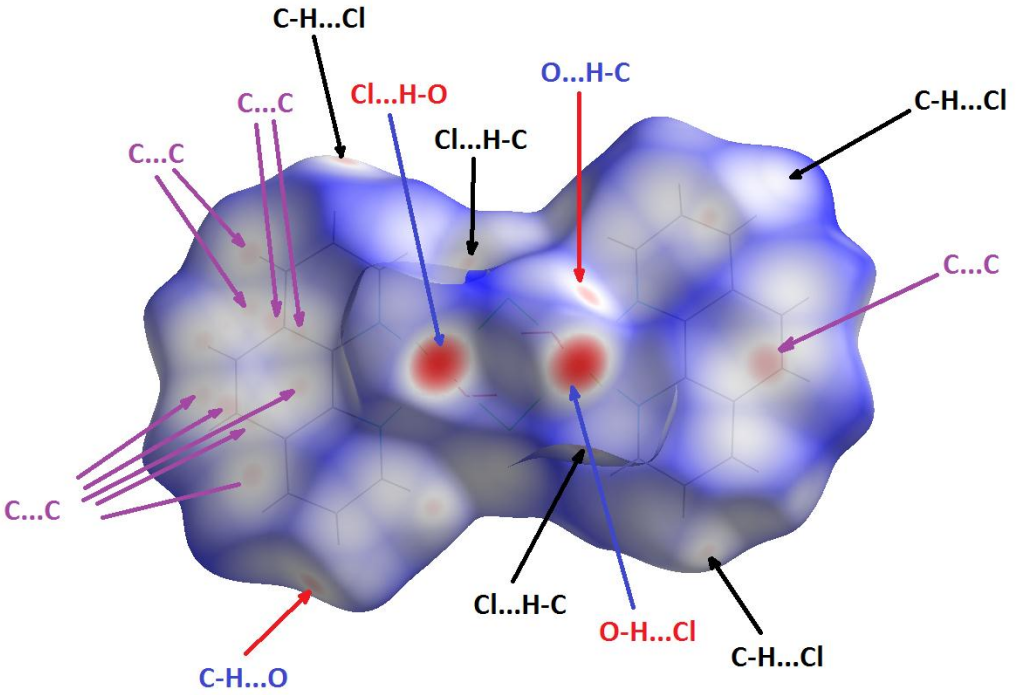
***Hirshfeld* surface analysis**

Cl…H/H…Cl , O…H/H…O and C…C contacts :

d_{norm} Representation



Asymmetric unit



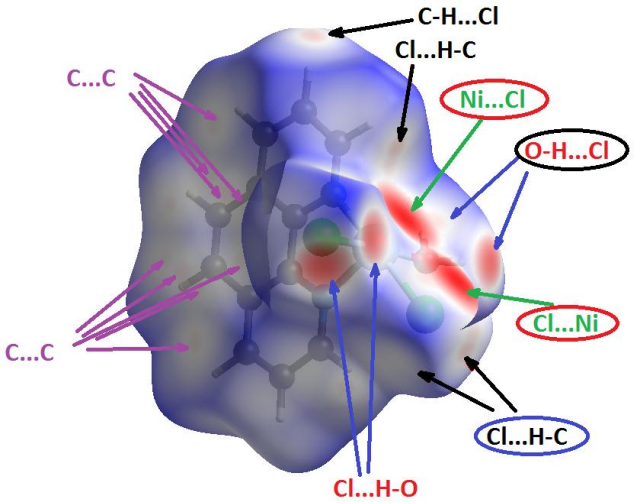
Binuclear complex

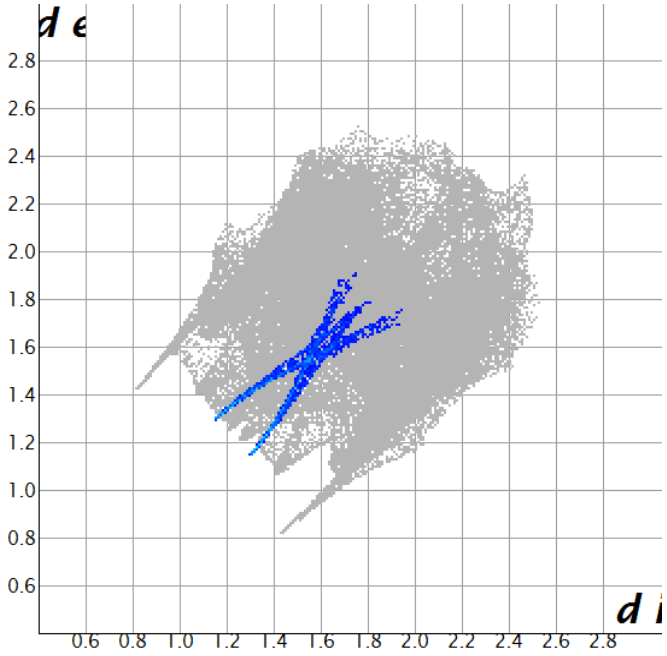
Results and discussion

Hirshfeld surface analysis

Cl…H/H…Cl , O…H/H…O and C…C contacts : d_{norm} Representation

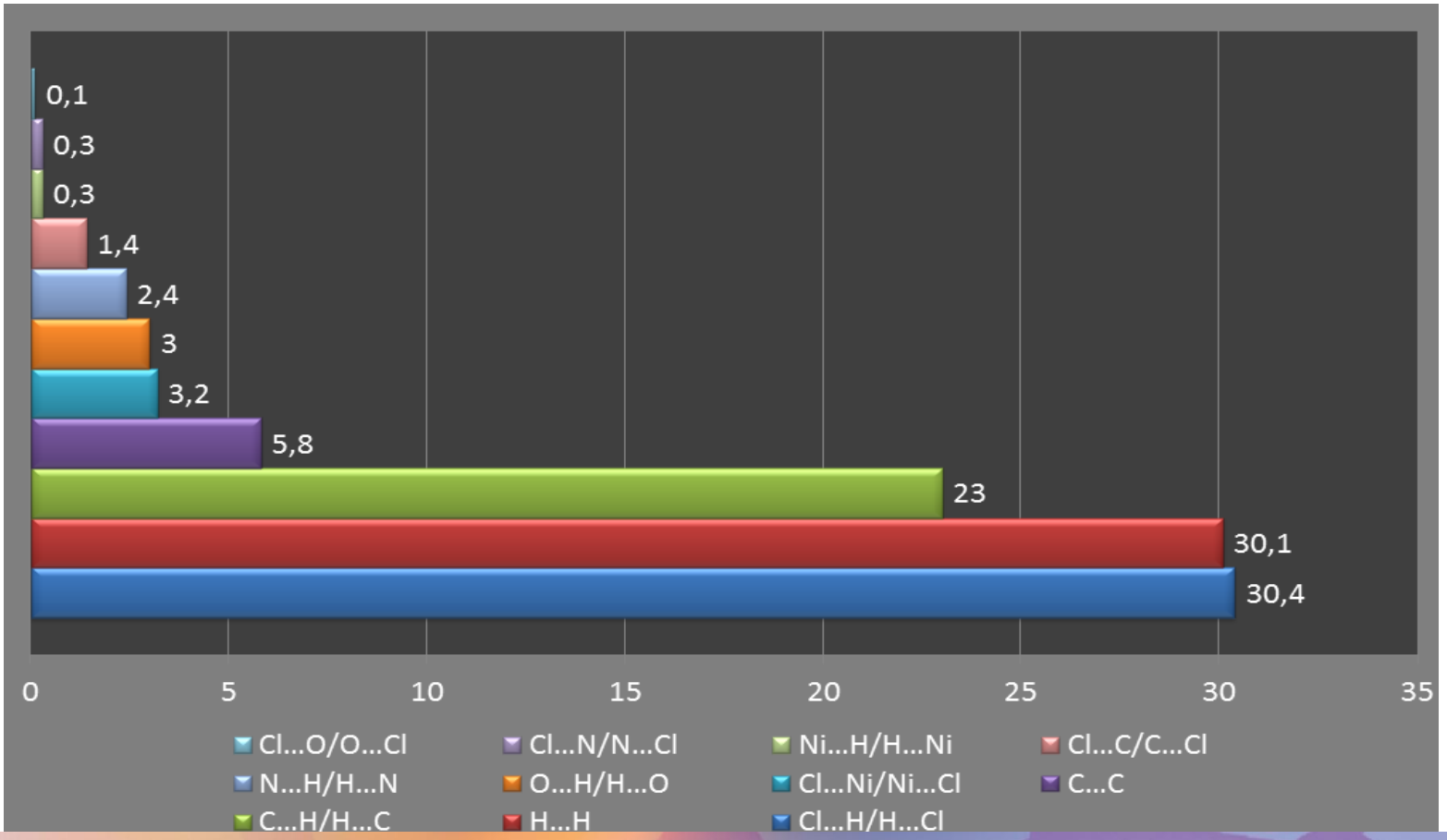
The consideration of the asymmetric unit in the HSA allowed visualizing the intramolecular non-covalent interactions in the Ni(II) complex, namely an extra C-H..Cl interaction, two extra O-H..Cl interactions and an intramolecular Ni..Cl interaction with a contribution to the total surface of 3.2%.





Results and discussion

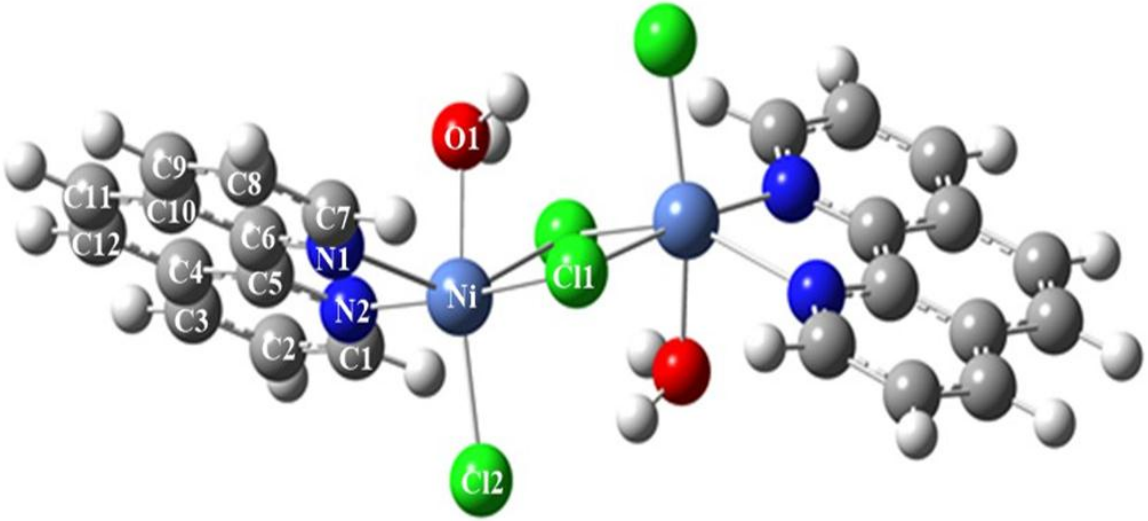
Hirshfeld surface analysis



Results and discussion

Quantum calculations
Optimized structure

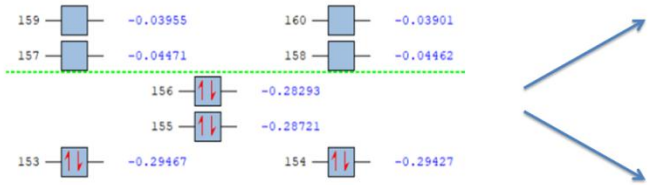
The structure was optimized by using one of the DFT function hybrids M06-2X method, with a mix basis set ; LANL2DZ was used for Ni^{2+} centers and 6-31G(d) for the other atoms in the complex

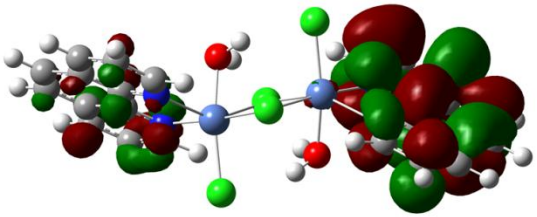


Results and discussion

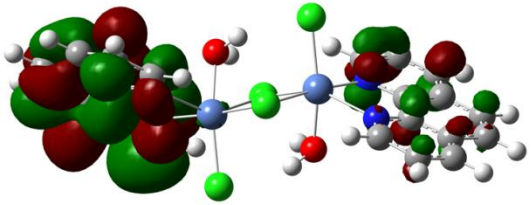
Quantum calculations

MOED and contour diagram :

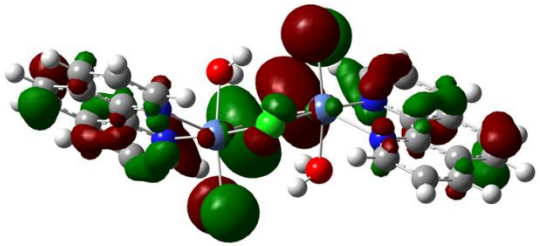




LUMO (157)



LUMO +1 (158)

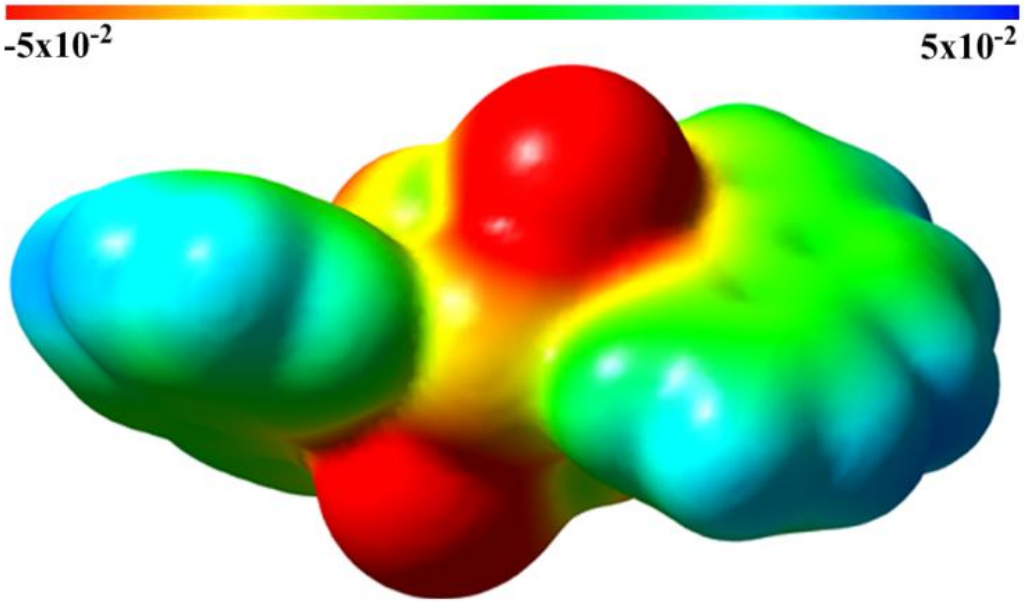


HOMO (156)

Results and discussion

Quantum calculations

MEP :



Conclusions

A binuclear phenanthroline-based nickel(II) complex was synthesized and characterized by single-crystal x-ray diffraction. Its crystal structure is made of $Ni_2Cl_4(H_2O)_2(Phen)_2$ dimmers linked to each other *via* intermolecular O-H…Cl hydrogen bonds. The non-covalent interactions in the binuclear framework were analyzed using*Hirshfeld* surface analysis which indicated a rich variety of non-covalent contacts namely : Cl…H/H…Cl, H…H, C…H/H…C, C…C, Ni…Cl/Cl…Ni, O…H/H…O, N…H/H…N and Cl…C/C…Cl. The quantum calculations were carried out and the optimized structural properties were examined in detail. Additionally, the active sites were determined by the calculation of contour plots of the molecular orbitals and the MEP map.

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