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Interactions energy, energy frameworks, *Hirshfeld* surface and topological analyses of a mononuclear Co(II) coordination framework

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Abstract:

A pyrazole-based Co(II) complex was synthesized and structurally characterized by means of single-crystal X-ray diffraction. The hydrogen-bonds and the non-covalent interactions within the complex analyzed by means of the *Hirshfeld* surface analysis showed the presence of N—H···Cl and C—H···Cl hydrogen-bonding networks in addition to weak non-classical H…H, N─H...C, C─H…N, N—H…π, π…*lp*/*lp*…π and *lp*…*lp* interactions. Additionally, the total energies of these intermolecular interactions were computed and the energy frameworks analyzed. The empty space in the crystal lattice using *void mapping* was also analyzed and showed the presence of small cavities. The structure was furthermore examined by means of topological analysis, which revealed the presence of 0-periodic binodal 1,6-connected **1,6M7-1** and 14-connected uninodal **bcu-x** topologies.

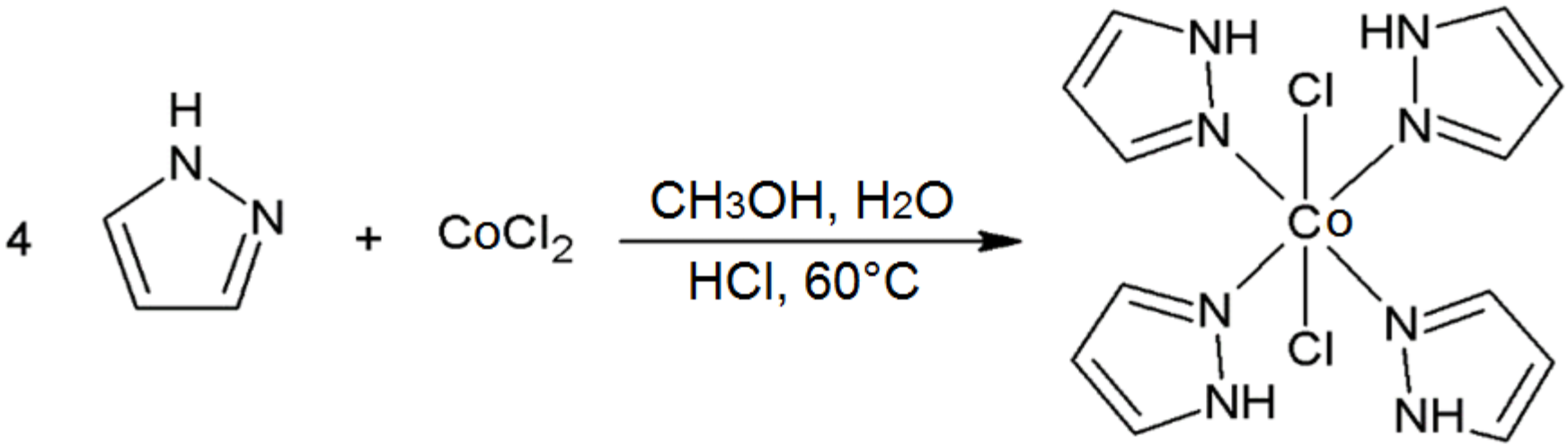
Keywords: Co(II) complex, intermolecular interactions, energy frameworks, *Hirshfeld* surface analysis, topological analysis.

Introduction

Heterocyclic ligands and their metallic complexes are biologically active materials [1–5], especially pyrazole-based ones, which are used in the pharmaceutical and agrochemical fields [6]. Accordingly, pyrazole-based copper and cobalt complexes showed excellent antibacterial and antifungal activities [7-9]. Particularly, the copper complexes were reported to have biological properties and some of them were active both *in vivo* and *in vitro* [9, 10]. On the other hand, many stable [M(Hpyrazole)$_4$X$_2$] complexes resulting from several transition metal cations with pyrazole and substituted-pyrazoles were reported [11-16]. In order to contribute to this complexes' family, a Co(II) complex, namely dichloro-tetrakis(1H-pyrazole)-cobalt(II) [17], was synthesized and structurally characterized by means of single-crystal X-ray diffraction. In this presentation, its hydrogen-bonds and non-covalent interactions will be explicitly analyzed by means of the *Hirshfeld* surface analysis. Additionally, in order to compute the total energies of the possible intermolecular interactions, the interactions energy and energy frameworks analyses' results will be discussed. The empty space in the crystal lattice will also be analyzed using *void mapping*. The structure will furthermore be examined by means of the topological analysis.

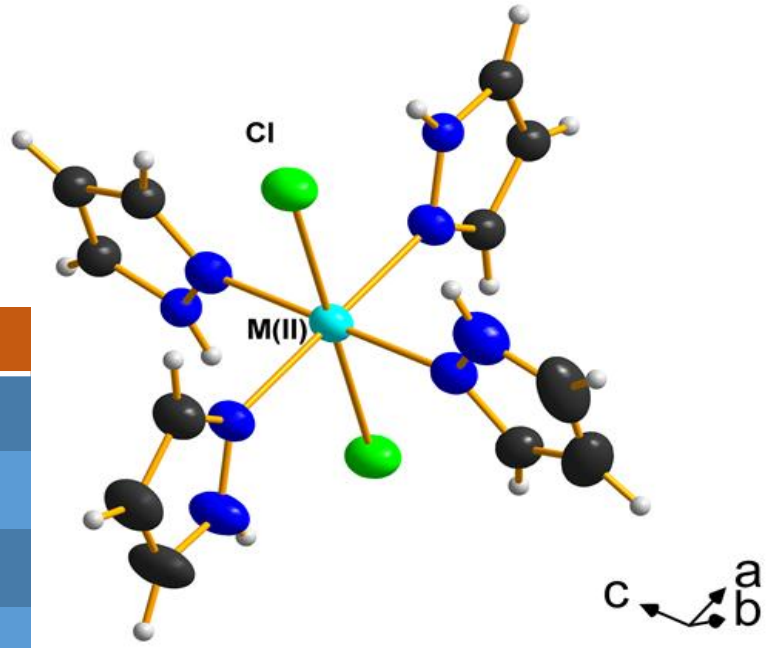
Results and Discussion

Synthesis :



Results and Discussion

Crystal structure :



Space Group	C2/c
a (Å)	13.6170(1)
b (Å)	9.2934(5)
c (Å)	14.9550(1)
β (°)	117.920(1)
$R[F^2 > 2\sigma(F^2)]$	0.0424
$wR(F^2)$	0.0952
$\Delta\varrho_{max}$, $\Delta\varrho_{min}$ (e $Å^{-3}$)	0.36, –0.30

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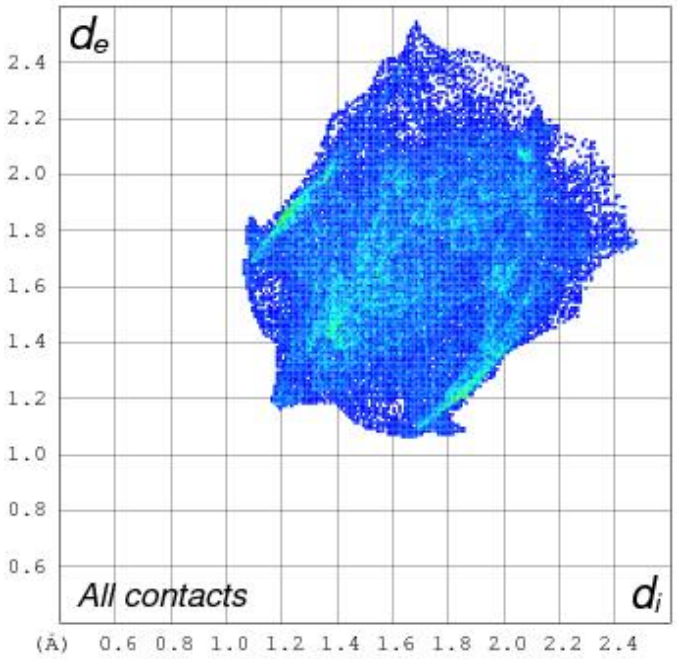
Results and Discussion

***Hirshfeld* surface analysis :**

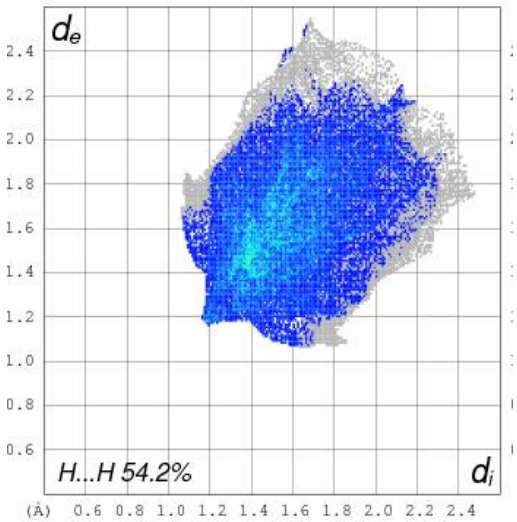
The *Hirshfeld* surfaces **HSs** and the fingerprint plots **FPs** of the cobalt complex were calculated using CrystalExplorer17 [18].

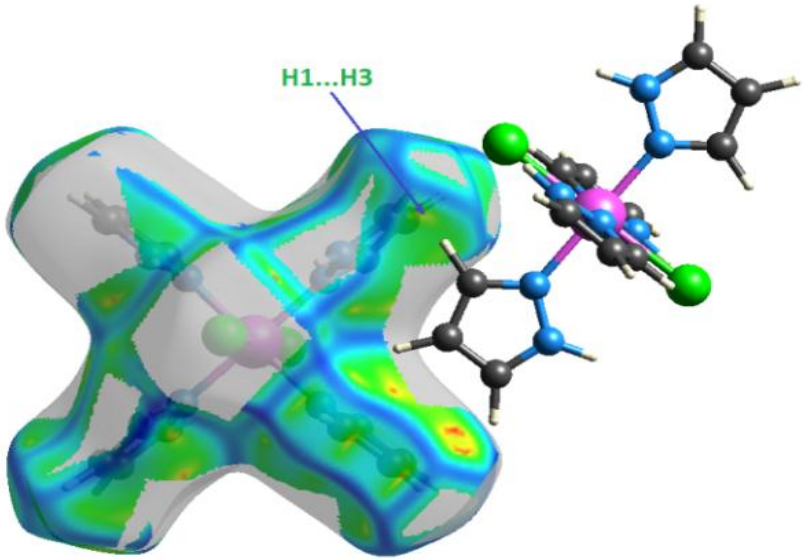


Results and Discussion

***Hirshfeld* surface analysis :**

The largest contribution over the total **HS** of 54.2% was observed for the H…H contacts, which are found to be located in the middle of the scattered points in the **FP** with a shortest distance corresponding to $d_e = d_i \sim 1.18$ Å and the close interaction C1—H1…H3—C3/C3—H3…H1—C1 highlighted on the *curvedness* representation.





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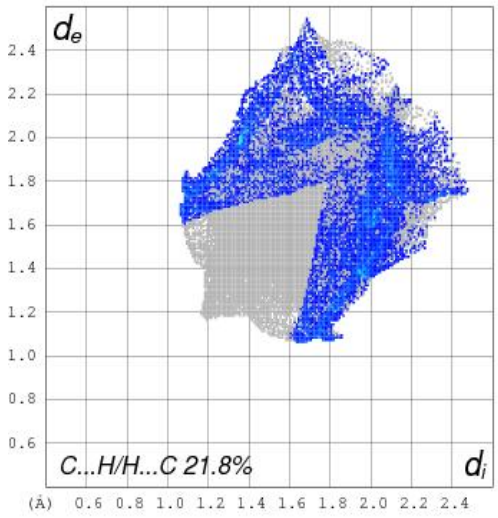
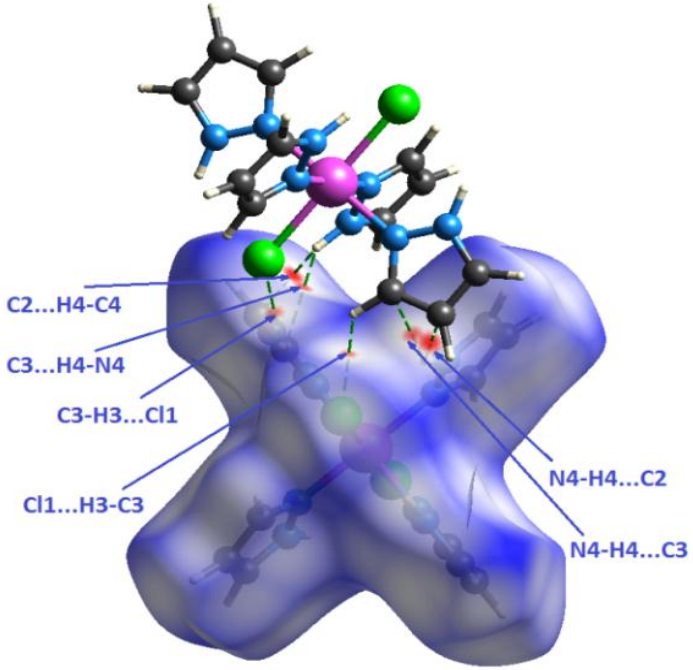
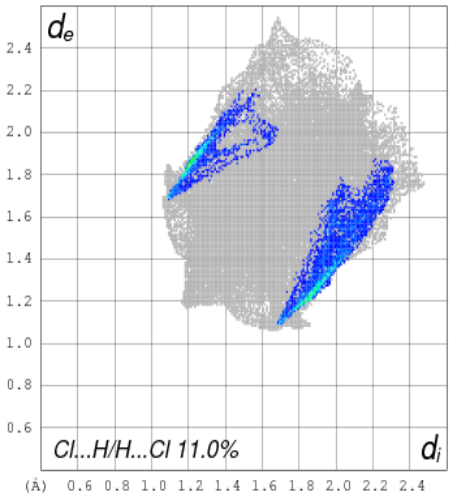
Results and Discussion

***Hirshfeld* surface analysis :**

The H…C/H…C (21.8%) and H…Cl/Cl…H (11.0%) contacts exhibit shortest interactions N4─H4…C2 and C3—H3…Cl1 appearing at about $d_e + d_i$ ~ 2.70 Å and ~ 2.80 Å .







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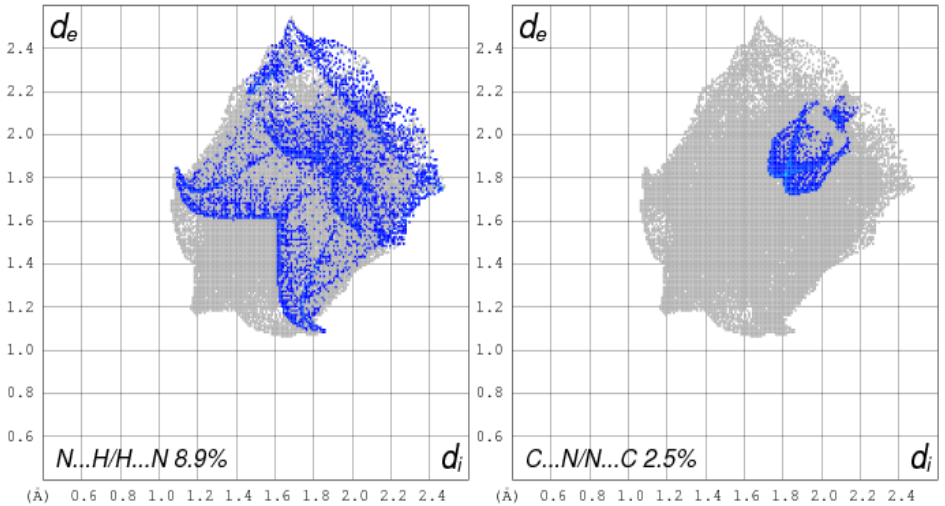
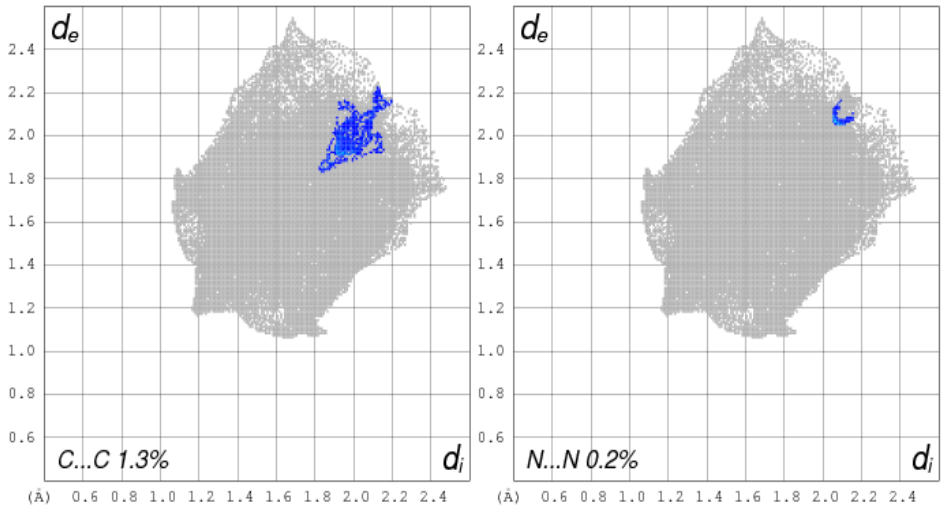
Results and Discussion

***Hirshfeld* surface analysis :**





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Results and Discussion

***Hirshfeld* surface analysis :**

- The shortest N…H/H…N contact (8.9%) results from the C4─H4…N2 interactions (~ 2.8 Å).

- The C…N/N…C (2.5%) and N…N (0.2%) contacts reflect the presence of the *van der Waals* π…*lp*/*lp*…π and *lp*…*lp* interactions, with shortest distances being respectively $d_e + d_i$ ~ 3.55 Å and $d_e = d_i$ ~ 2.5 Å.

- The C…C contacts (1.3%) exhibit a closest ring centroid-to-ring centroid distance of about 3.68 Å.

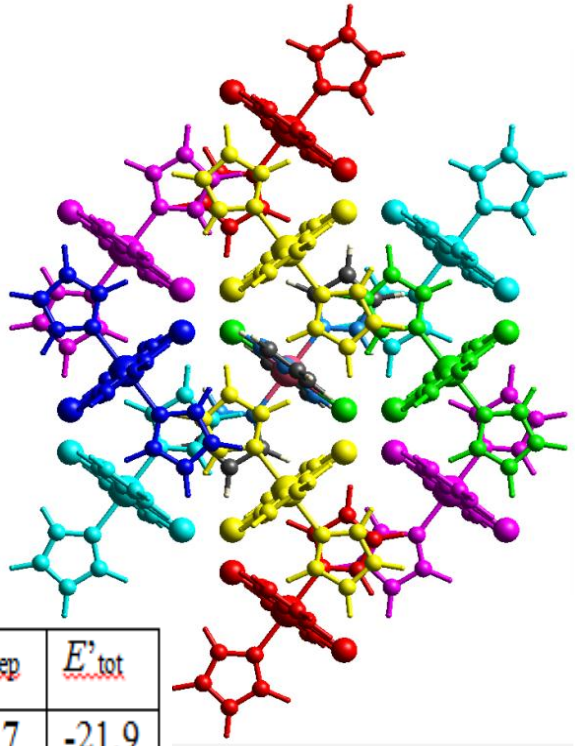
Results and Discussion

Energy frameworks analysis :

- The interaction energies **IEs** and the energy frameworks **EFs** [19] of the studied complex were calculated using CrystalExplorer17 [18].
- The total energies of the possible intermolecular interactions are in the range [−0.5, −41.1] kJ·mol^{-1}.
- The *lattice energy* for the complex is found to be −191.4 kJ·mol^{-1}.

Results and Discussion

Energy frameworks analysis :

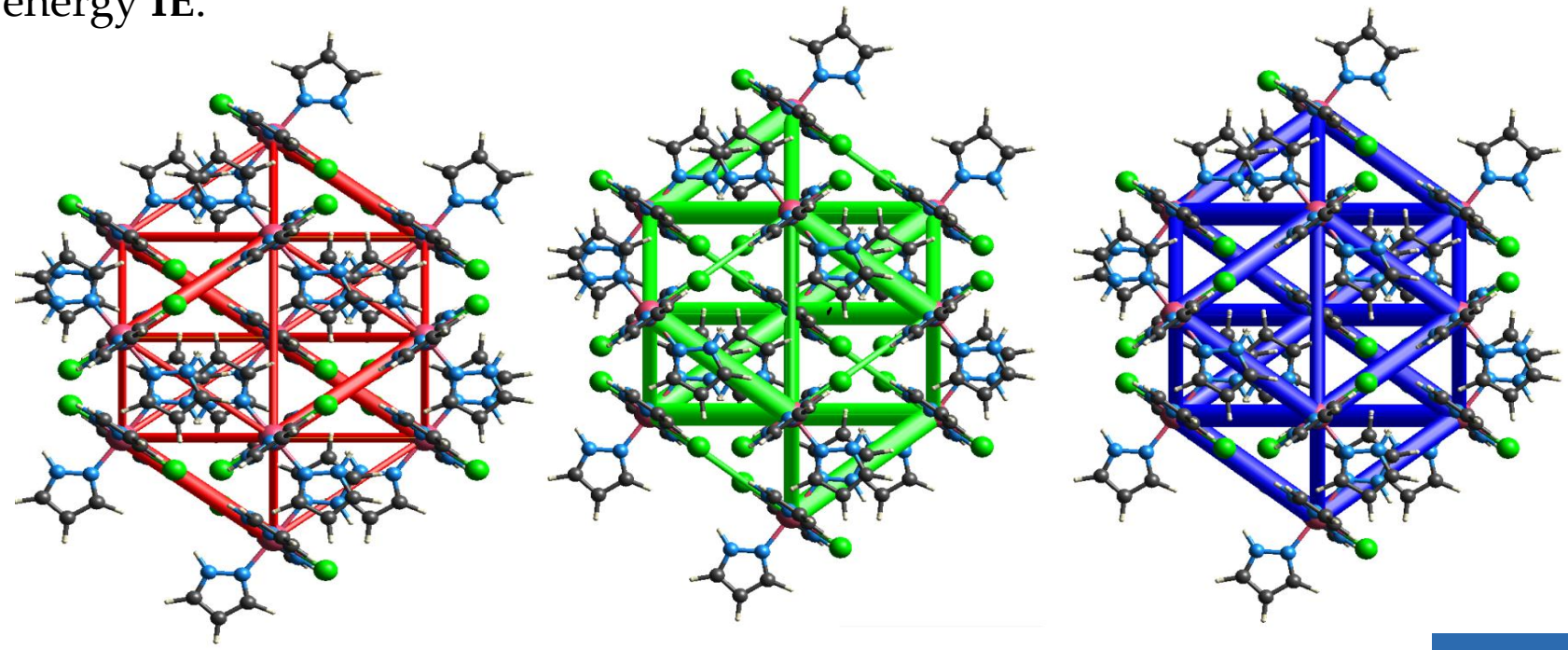


	N	Primary interaction	Symmetry code	*R*	*E'*ele	*E'*pol	*E'*dis	*E'*rep	*E'*tot
	2	H…H	*x*, *y*, *z*	9.29	-12.2	-3.5	-15.6	11.7	-21.9
	4	C–H…Cl, H…H	-*x*+½ ,*y*+½, -*z*+½	8.80	-8.2	-2.2	-29.2	17.5	-24.9
	2	N—H…π, C–H…Cl	-*x*, *y*, -*z*+½	7.39	-16.9	-8.9	-46.6	39.9	-40.4
	2	C—H…π, C—H…*lp*	*x*+½ ,*y*+½, *z*	8.24	-11.1	-2.7	-49.5	31.0	-37.7
	2	π…π, C—H…π	-*x*, *y*, -*z*+½	12.25	1.1	-0.1	-1.8	0.0	-0.5
	2	N–H…Cl	*x*+½ ,*y*+½, *z*	8.24	-28.0	-6.5	-13.9	8.7	-41.1

Results and Discussion

Energy frameworks analysis :

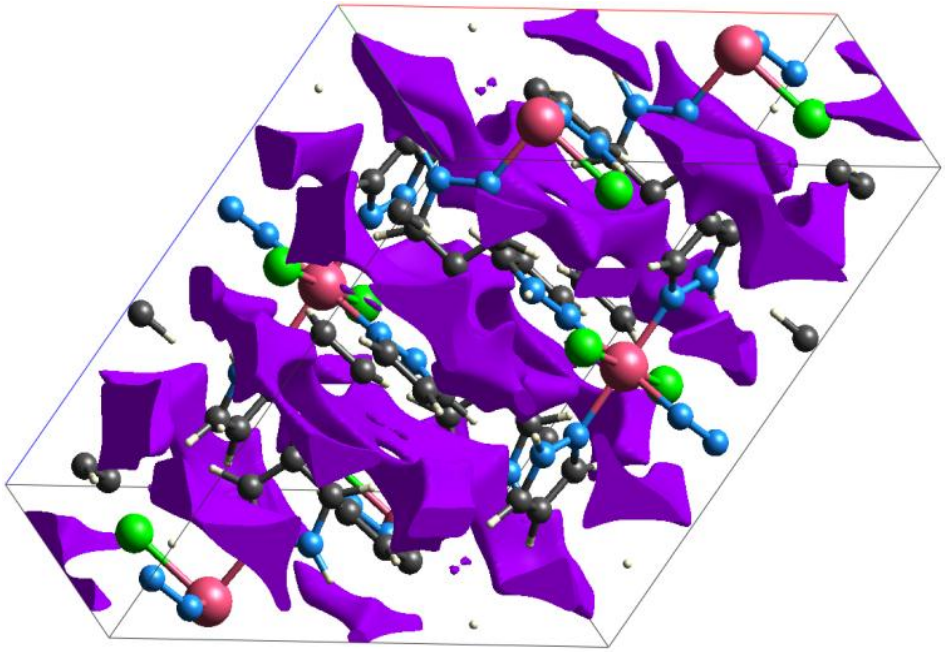
Electrostatic, dispersion components and their corresponding total interaction energy **IE**.



Results and Discussion

Voids :

The *surface area* is found to be 546.66 Å^2 and the calculated *voids volume* is 141.35 Å^3, while the volume of the unit cell is 1672.2 Å^3 which indicates that the voids percentage of the unit cell is only worth 8.45%.



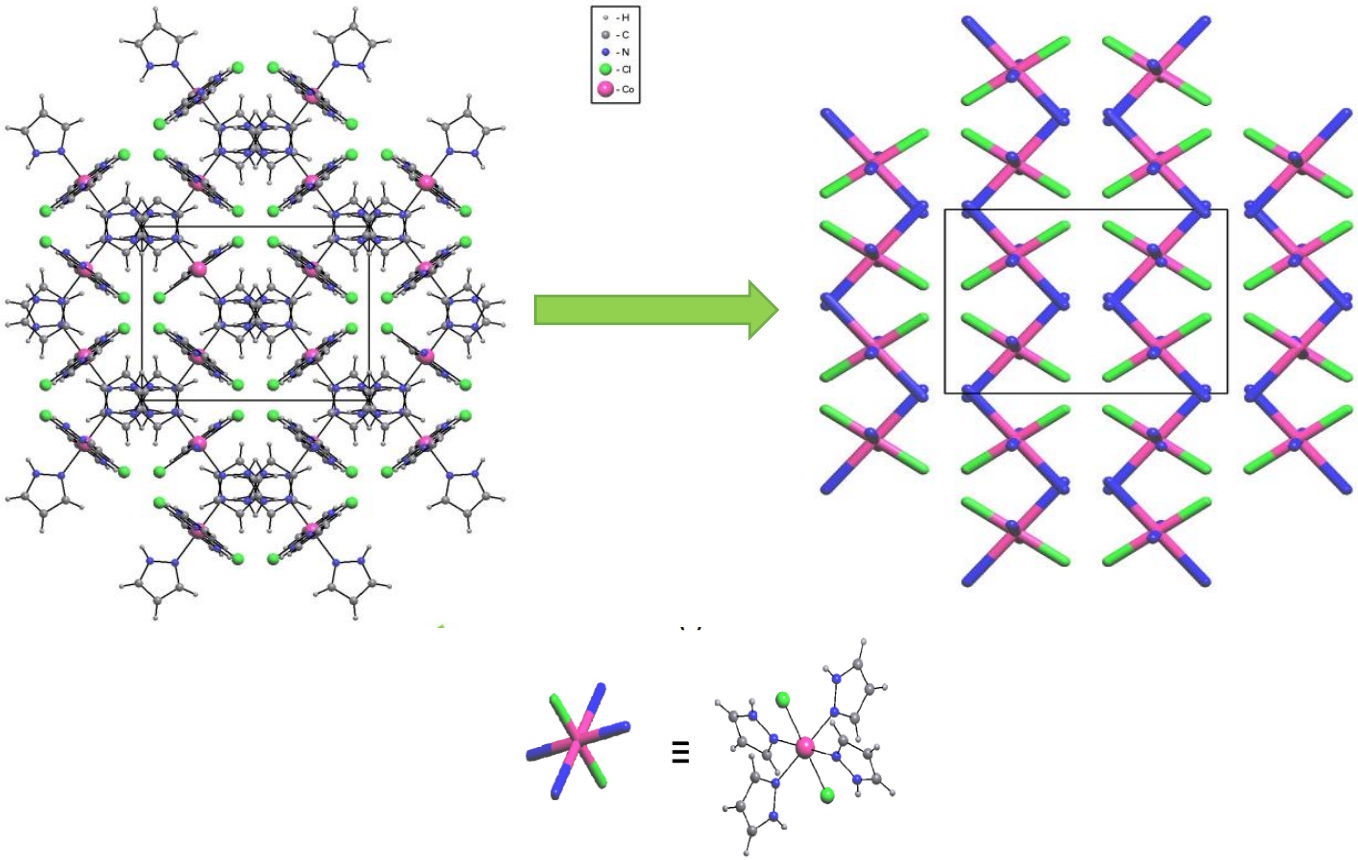
Results and Discussion

Topological analysis :

The topological studies were performed using the software package ToposPro [20]. The *standard representation* of the studied complex analyzed over the *standard representation of coordination compounds and valence-bonded MOFs* was performed by taking into account the cobalt cations, the pyrazole ligands and the counter-ions as the central nodes of the net, where the nodes are the gravity centers of each unit, gave a 0-periodic binodal 1,6-connected **1,6M7-1** underlying net, with stoichiometry $(1\text{-c})_6(6\text{-c})$.

Results and Discussion

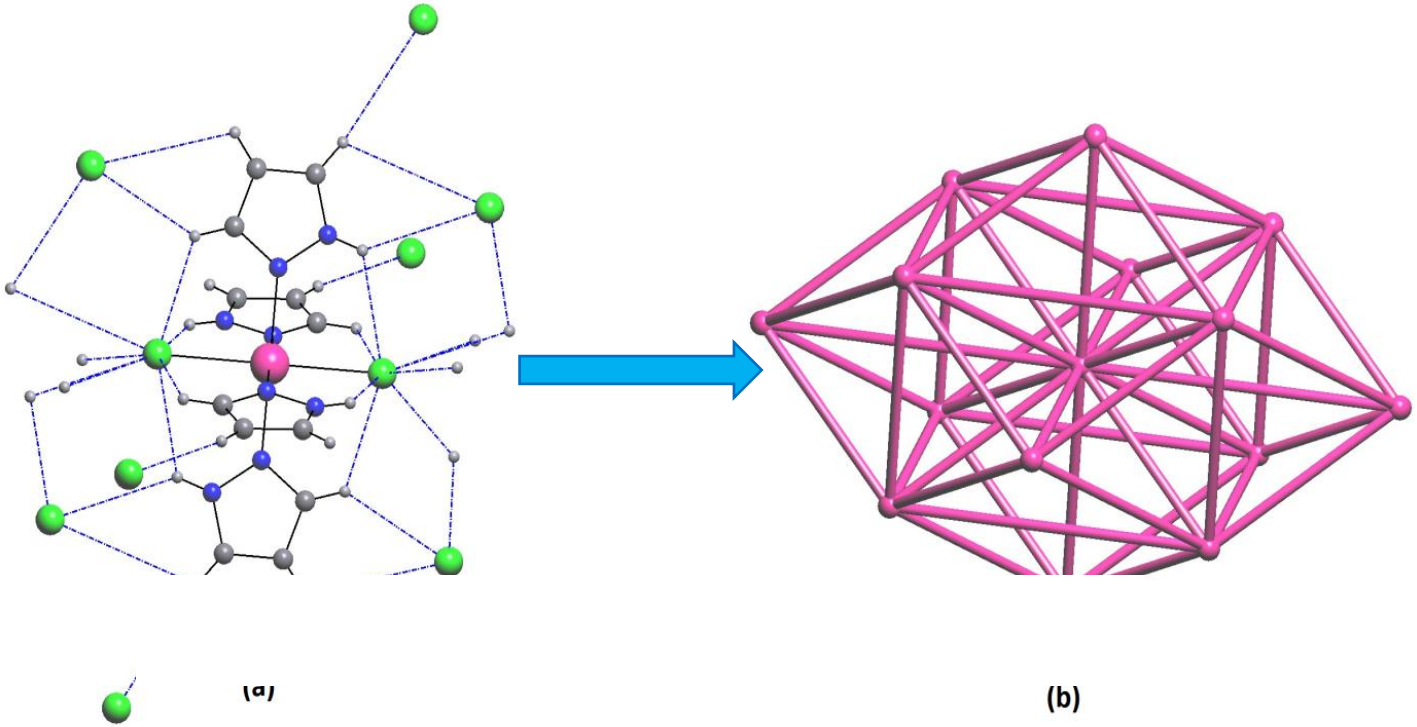
Topological analysis :



Results and Discussion

Topological analysis :

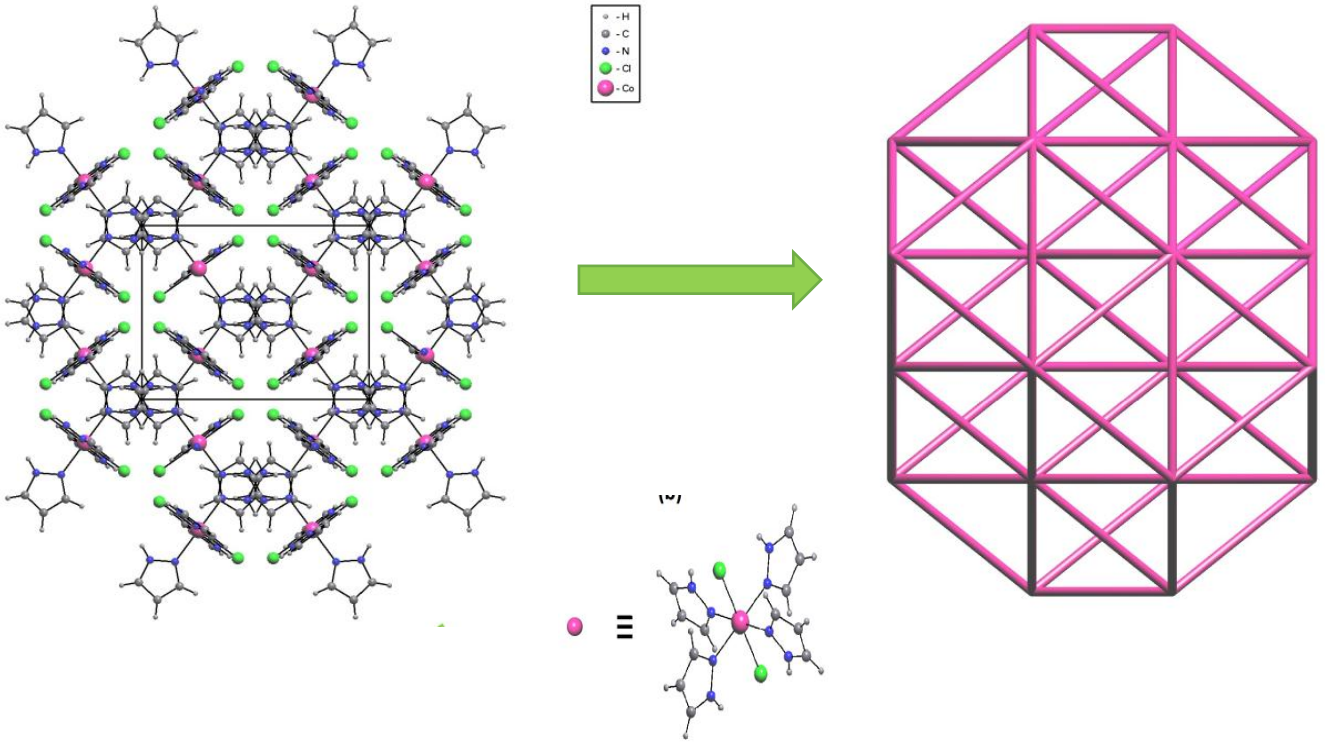
The structure could be analyzed over another simplified description by adopting the same *simplification* means of the molecular structure linked through all the existing hydrogen bonds and *van der Waals* interactions built up from the counter-ions as acceptors regarded as 14-connected nodes.



Results and Discussion

Topological analysis :

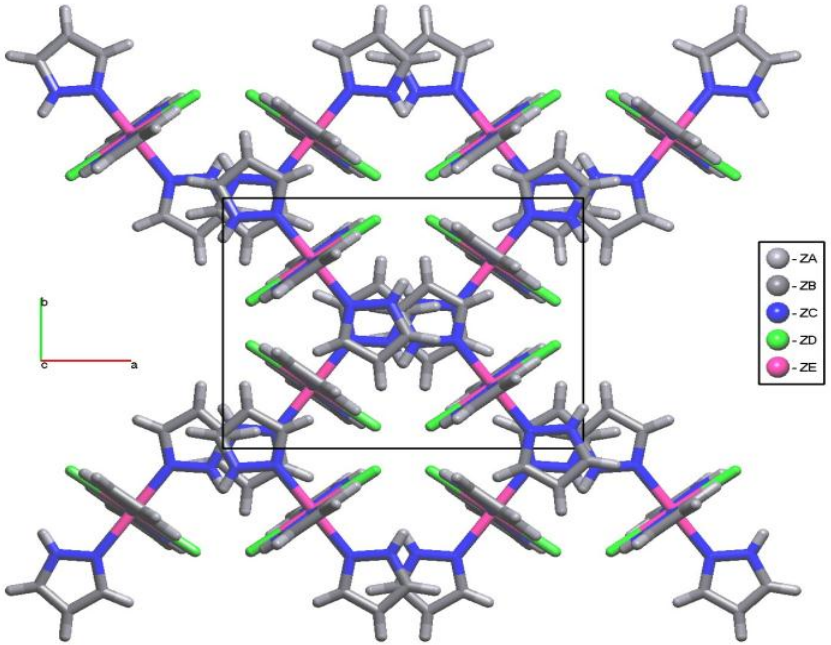
Furthermore, the same *simplification* concept resulted in a reduced 14-connected uninodal body-centered cubic **bcu-x** net [21] (**sqc38** : EPINET [22]), with the point symbol ($3^{36}.4^{48}.5^{7}$).



Results and Discussion

Topological analysis :

The *standard representation of covalent and ionic compounds* obtained by considering the centroids of each atomic entity composing the complex, the structure could be simplified to a new topological 7-nodal $1^3,3^3$,6-connected underlying net, with the $(1\text{-c})_8(1\text{-c})_8(1\text{-c})_2(3\text{-c})_8(3\text{-c})_8(3\text{-c})_4(6\text{-c})$ stoichiometry.



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Conclusions

The studied material investigated by means of the *Hirshfeld* surface analysis showed the presence of non-classical H…H, N─H...C, C─H…N interactions and N—H…π, π…*lp*/*lp*…π, *lp*…*lp van der Waals* forces in addition to the N—H···Cl and C—H···Cl hydrogen-bonding networks. The strength of these framework interactions were furthermore estimated by studying their types and their energies. Additionally, the empty space in the crystal lattice was analyzed *via* the *void mapping* and revealed the presence of small cavities. On the other hand, the topological analysis indicated that the discrete [MPz_4Cl_2] units are linked together through weak inter- and intramolecular N—H···Cl and C—H···Cl hydrogen bonds forming a 14-connected uninodal **bcu-x** topology.

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Acknowledgments

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