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A pyrazole-containing copper coordination framework : an investigation into its *Hirshfeld* surface analysis, magnetic behavior and biological activity

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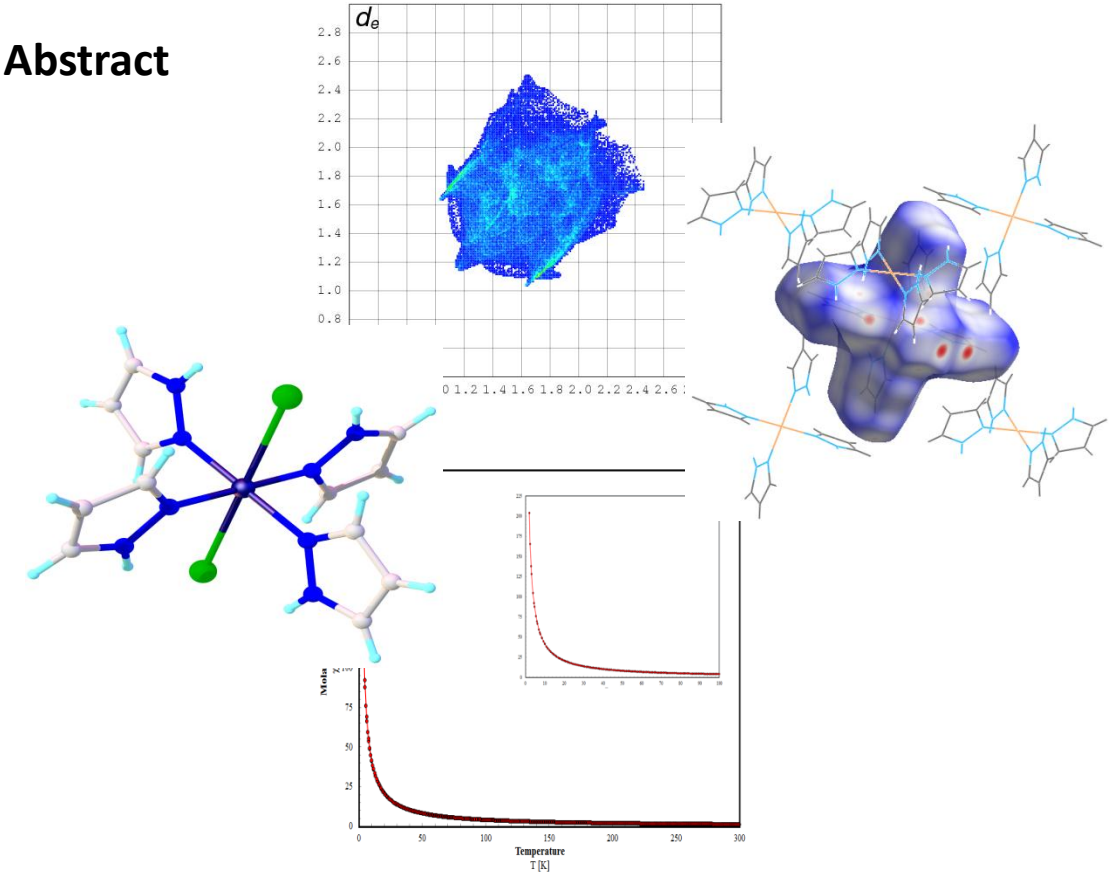
LASPI²A

A pyrazole-containing copper coordination framework : an investigation into its *Hirshfeld* surface analysis, magnetic behavior and biological activity

Graphical Abstract



Abstract:

The pyrazole derivatives have been widely used to design materials and complexes with interesting intermolecular interactions and properties. The pyrazole-based complex : *trans*-Dichlorotetrakis (1*H*-pyrazole-κN^2)copper(II) is structurally characterized by means of FT-IR spectroscopy and single-crystals X-ray diffraction. Its magnetic and biological properties are investigated for the first time, showing no particular magnetic behavior and a promising antifungal activity. Moreover, the *Hirshfeld* surfaces used to define the intermolecular environment of the molecules within the crystal together with the 2D-figerprint graphics allowing exploring the properties and the occurrence of each intermolecular contact in the studied complex are discussed in detail and showed the presence of N–H…Cl, C–H…Cl, C–H…π and other unconventional intermolecular interactions.

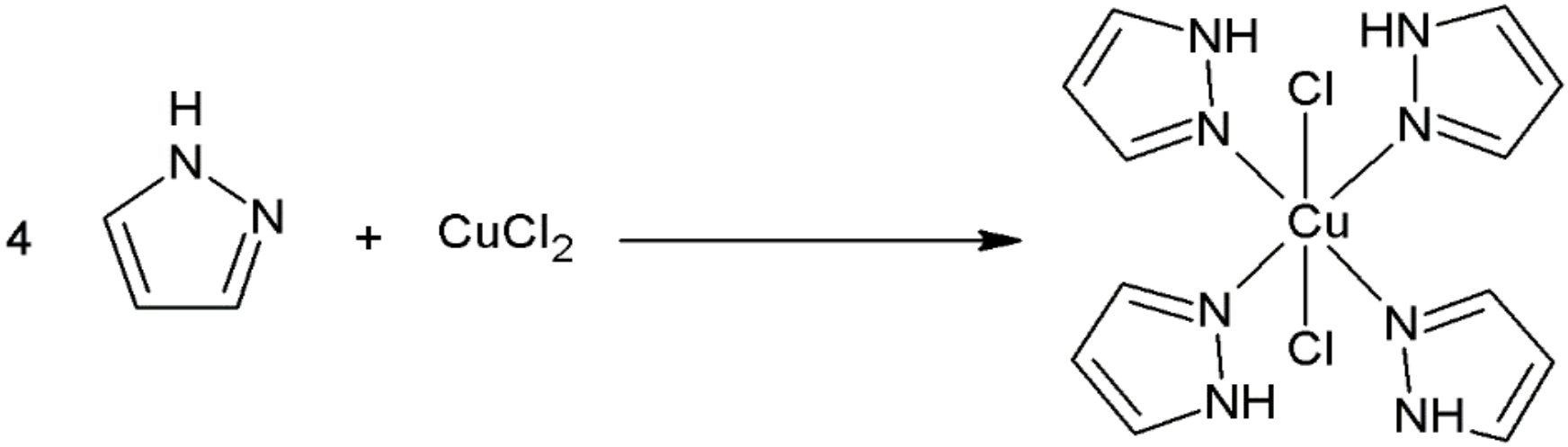
Keywords: Pyrazole-containing complexes, MOFs, intermolecular interactions, *Hirshfeld* surface analysis, magnetic properties, biological activity.

Introduction

Metal organic frameworks (MOFs) consist of metal ions or clusters often coordinated to rigid organic molecules to form one-, two-, or three-dimensional structures. Pyrazole ligands have been widely used in order to build new MOFs and their properties and applications have been extensively investigated [1-3]. Therefore, the properties of pyrazole-based systems have been studied due to their chelating ability with metallic ions as terminal ligands, bridging ligands and precursors for the design of several multi-nitrogen ligands for coordination, bioinorganic and organometallic chemistry [4], in order to build up new coordination polymeric networks and metal-organic frameworks. Additionally, they are well known for their spin-crossover behavior and their biological and medicinal properties as analgesic, anti-inflammatory agents [5], etc. As a contribution to what has been previously reported, we will be describing herein, for the first time, the magnetic properties and the antimicrobial activity of a pyrazole-based copper complex [6]. Furthermore, the *Hirshfeld* surfaces and the 2D-figerprint graphics [7] allowing the understanding of the properties and the occurrence of each intermolecular contact around the studied complex molecules will be discussed exclusively in detail.

Results and discussion

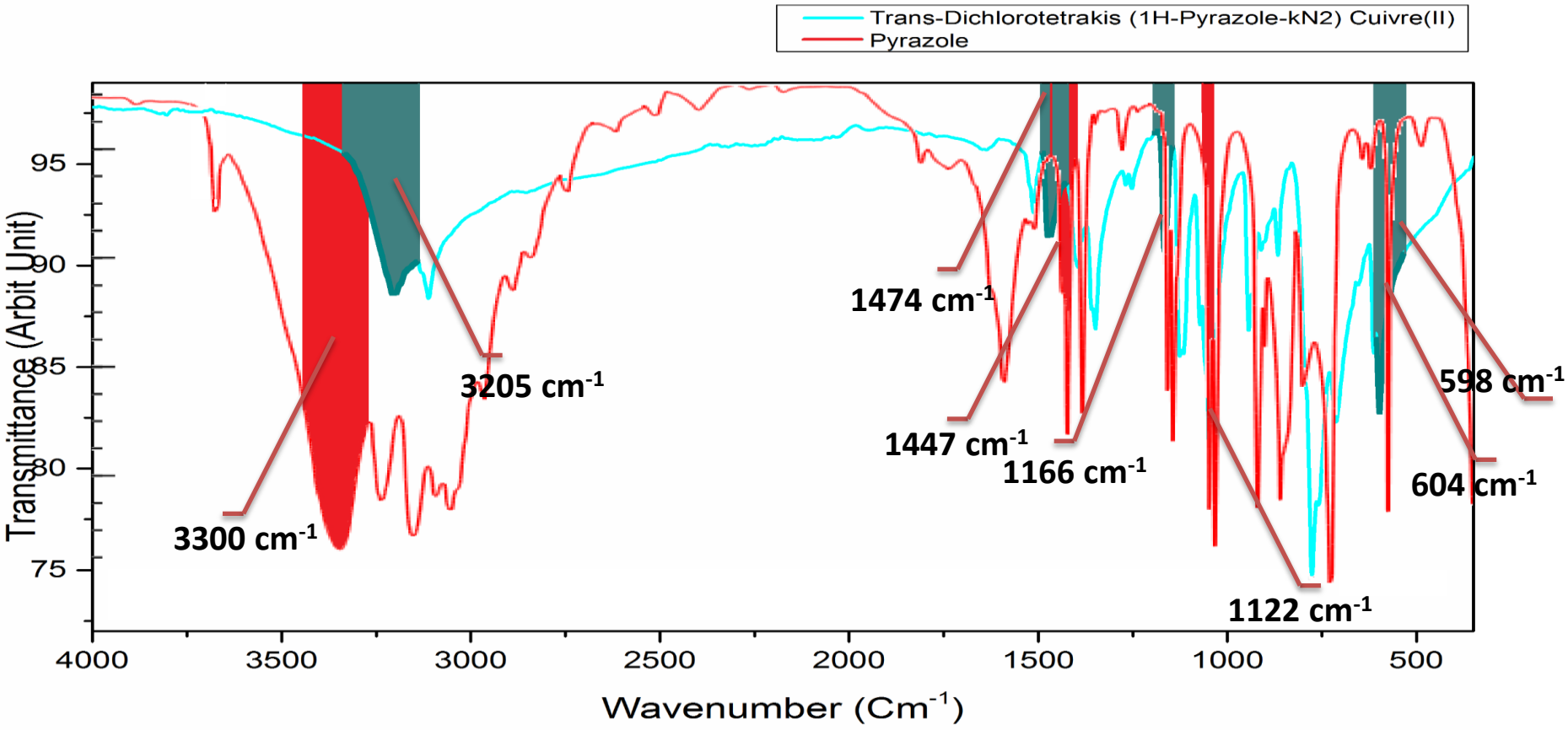
Synthesis



(1)

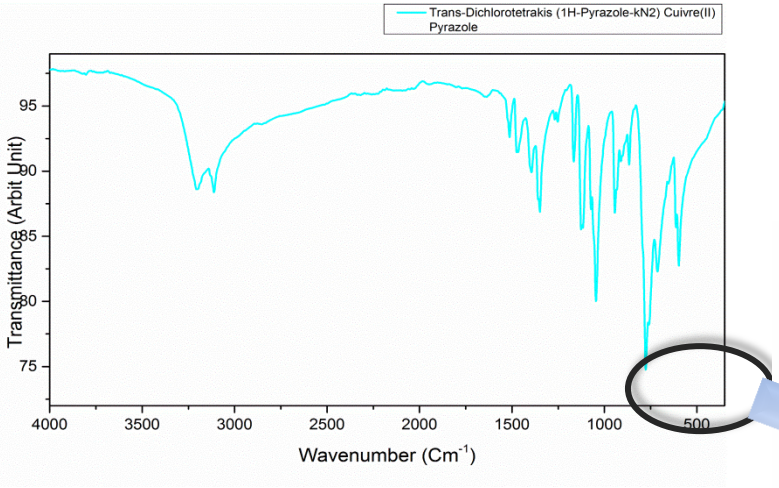
Results and discussion

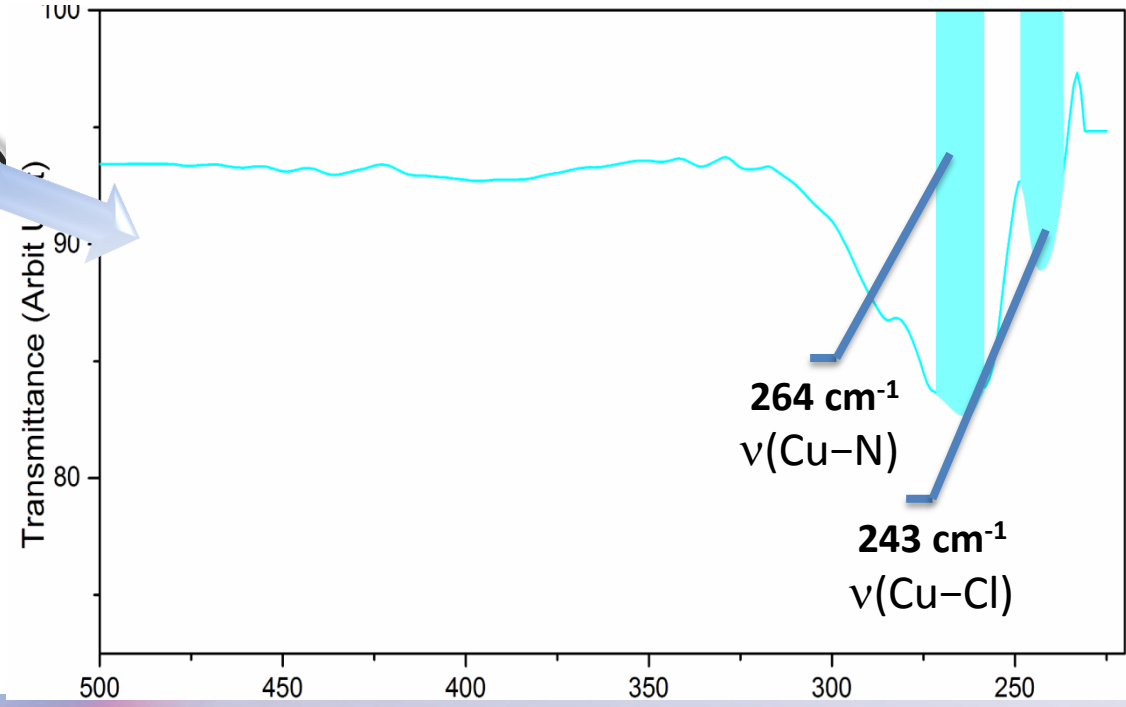
FTIR spectroscopy



Results and discussion

FTIR spectroscopy

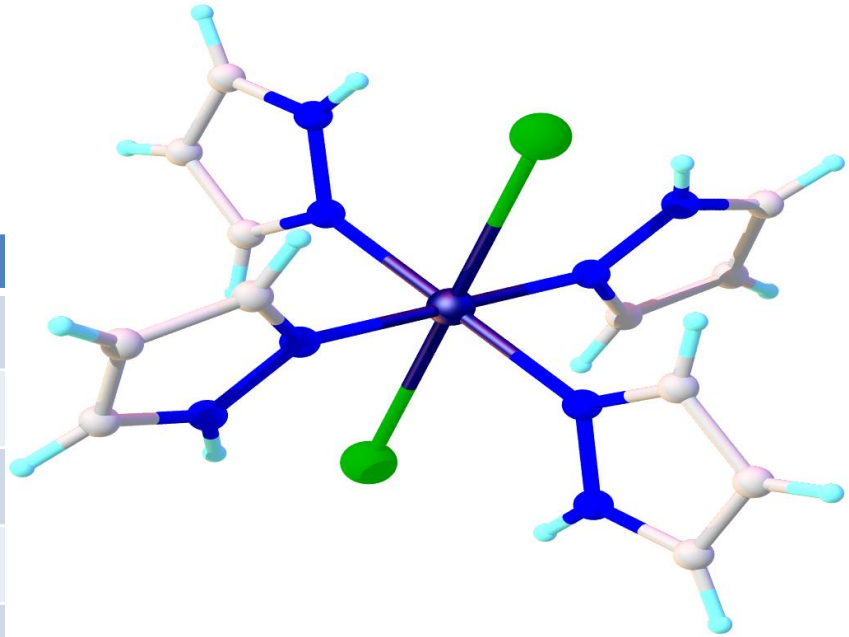




Results and discussion

Crystal structure

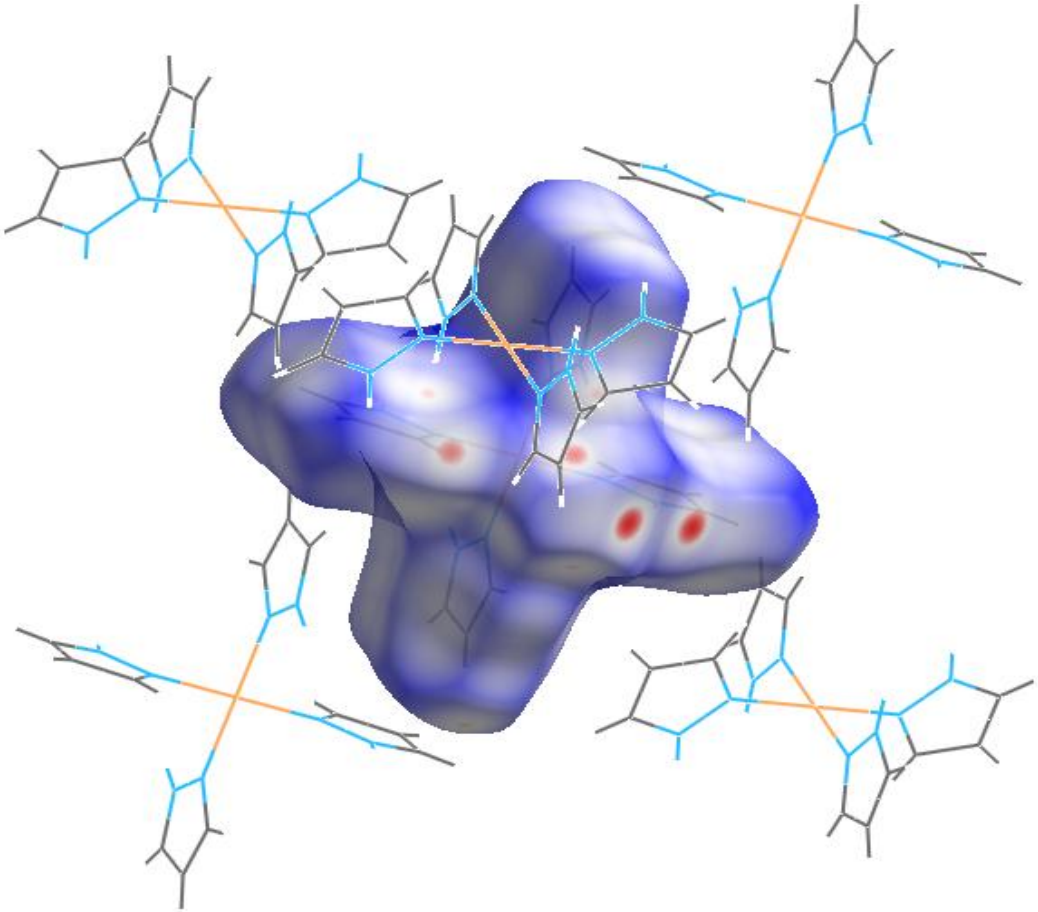
Space Group	*C*2/*c*
a (Å)	13.5430(10)
b (Å)	9.1480(10)
c (Å)	14.6480(10)
β (°)	116.700(5)
$R[F^2 > 2\sigma(F^2)]$	0.025
$wR(F^2)$	0.069
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e $Å^{-3}$)	0.34, –0.29



(1)

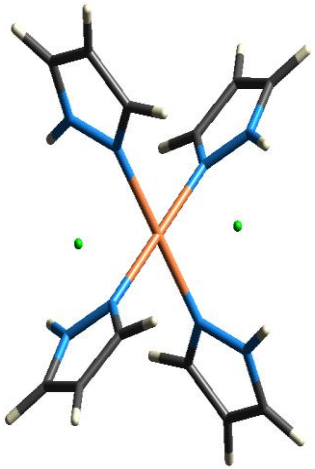
Results and discussion

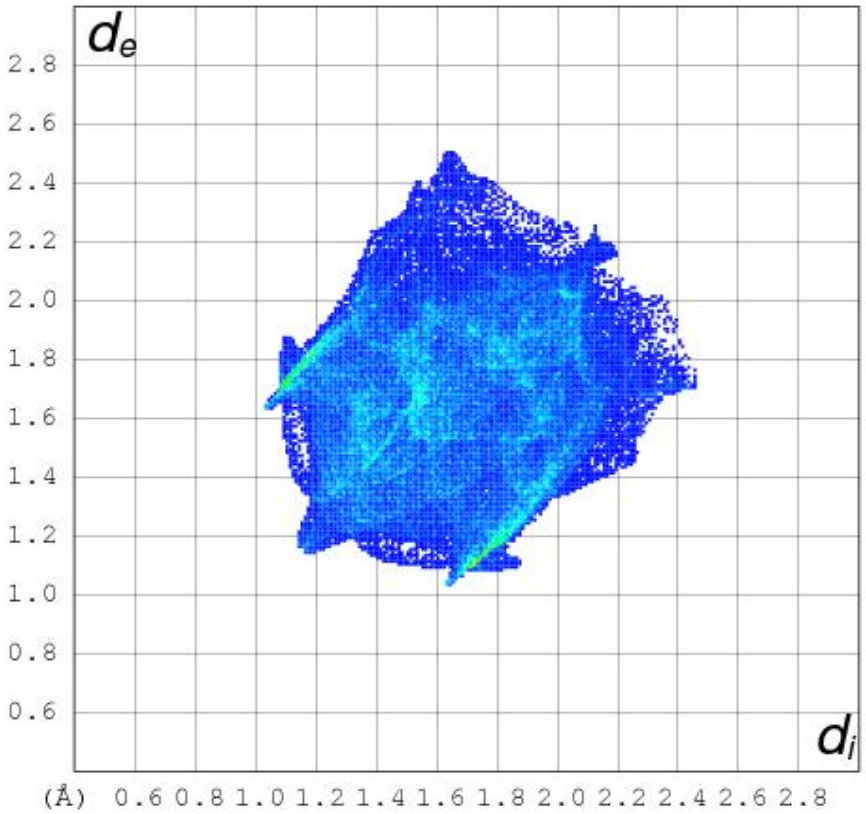
Hirshfeld suraface analysis



Results and discussion

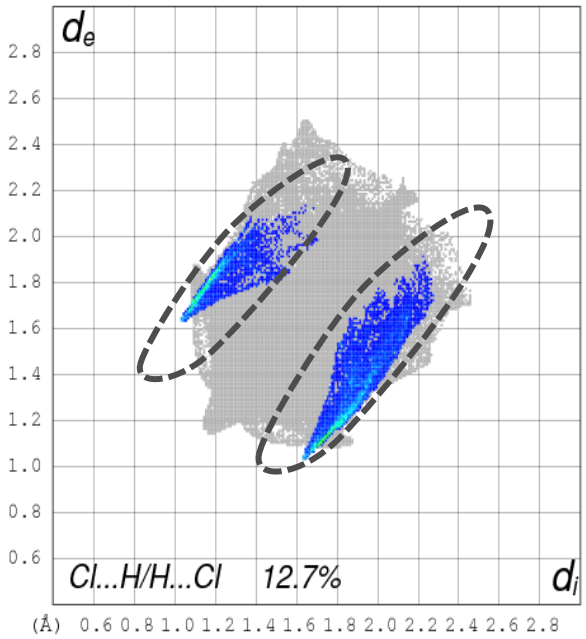
Hirshfeld suraface analysis
Fingerprint plots

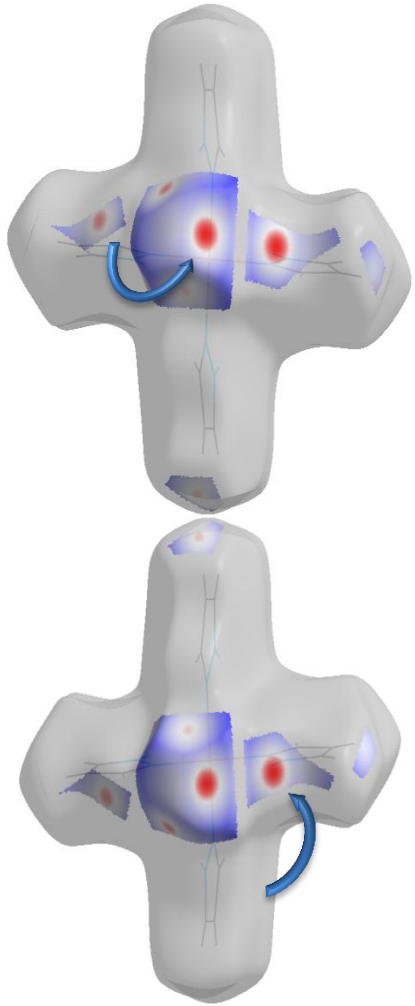




Results and discussion

Hirshfeld suraface analysis
Cl…H/H…Cl Contacts





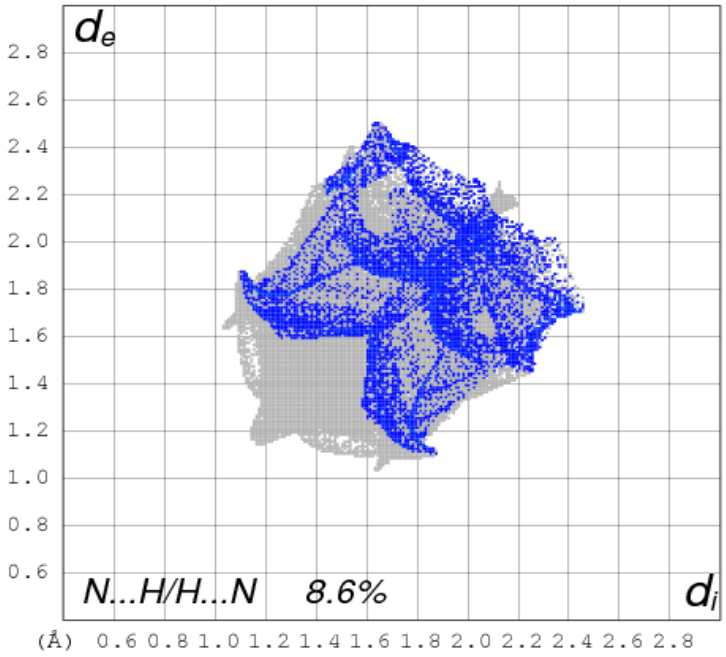
8 Contacts

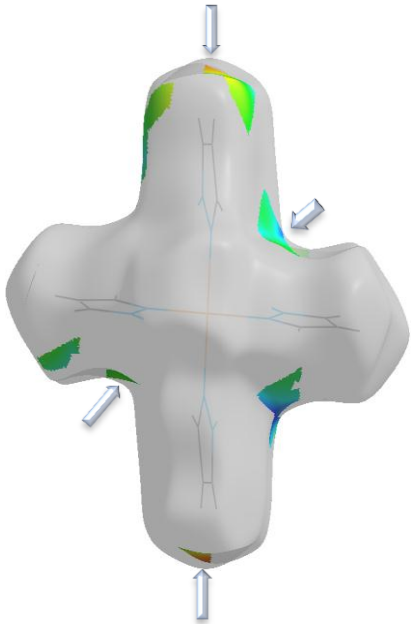
- 3 C–H…Cl
- 1 N–H…Cl

N4–H4N…Cl1 (2.64 Å)

Results and discussion

Hirshfeld suraface analysis
N…H/H…N Contacts





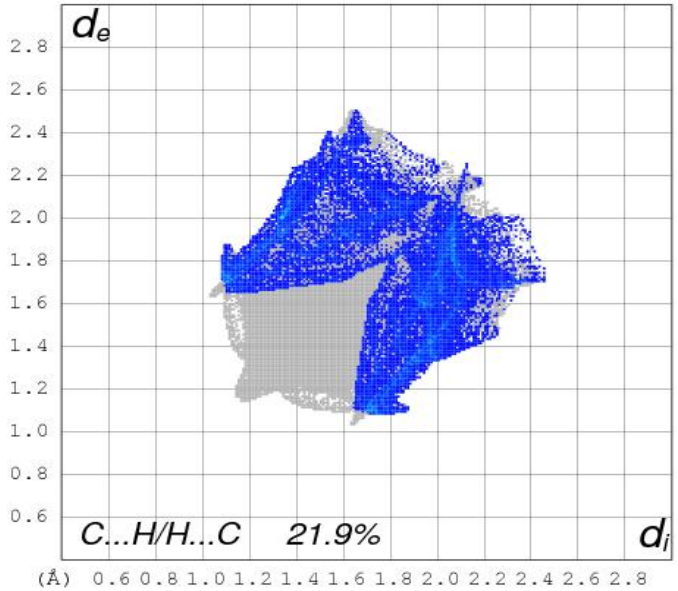
10 Contacts

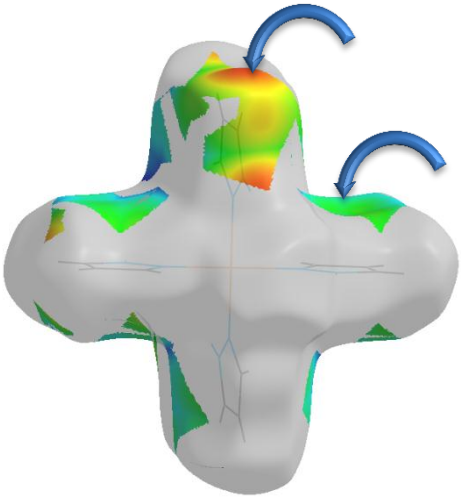
- 5 C–H…N

C1–H1…N1 (2.85 Å)

Results and discussion

***Hirshfeld* suraface analysis**
C…H/H…C Contacts

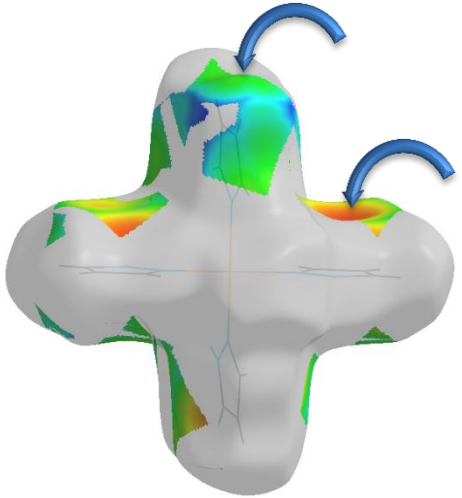




12 Contacts

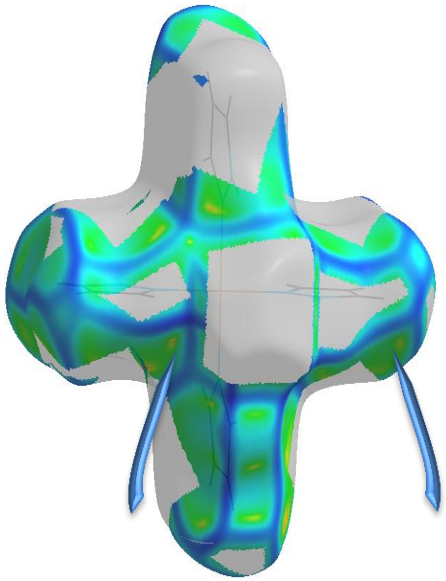
- 3 N–H…C
- 3 C–H…π

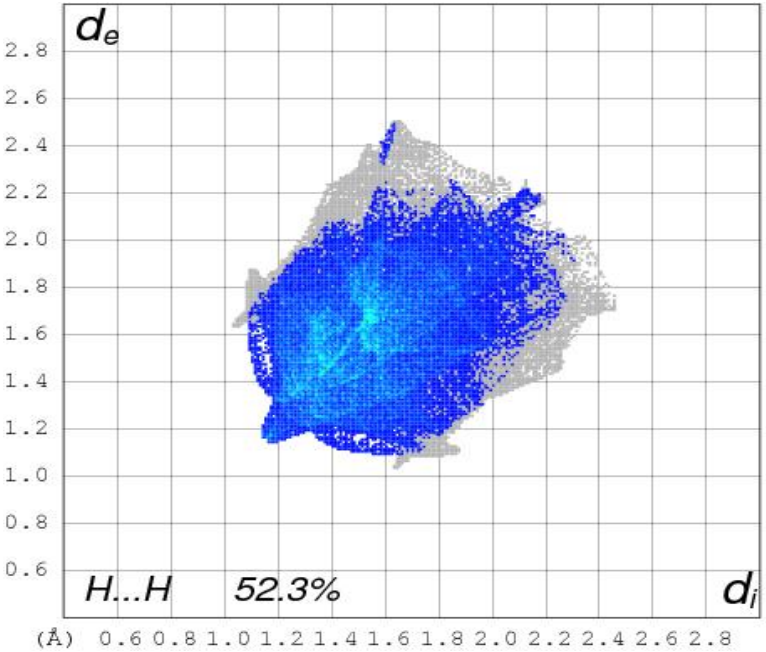
C1–H1…π *(2.80 Å)*



Results and discussion

Hirshfeld suraface analysis
H…H Contacts





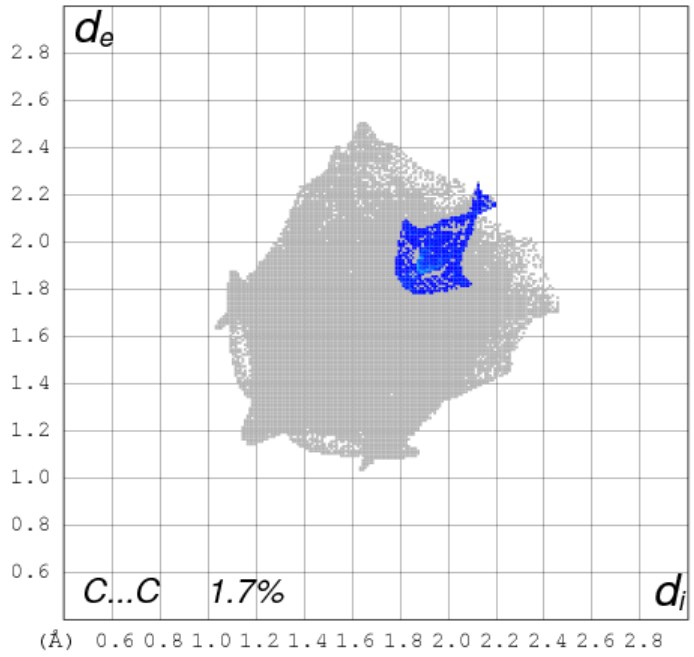
15 Contacts

- 5 C–H…H–C
- 3 C–H…H–N

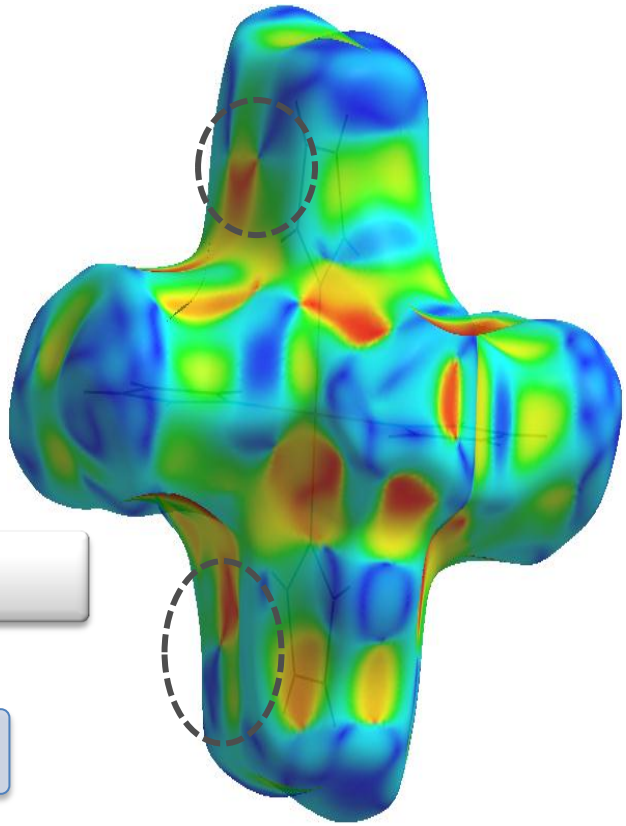
C4–H4…H6–C6 *(2.33 Å)*

Results and discussion

Hirshfeld suraface analysis
C…C Contacts



π…π (3.60 Å)

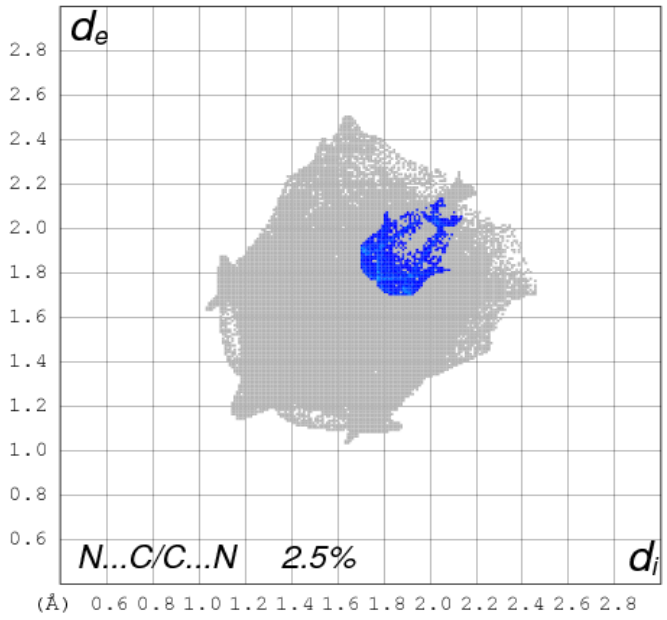


4 Contacts

2 π…π

Results and discussion

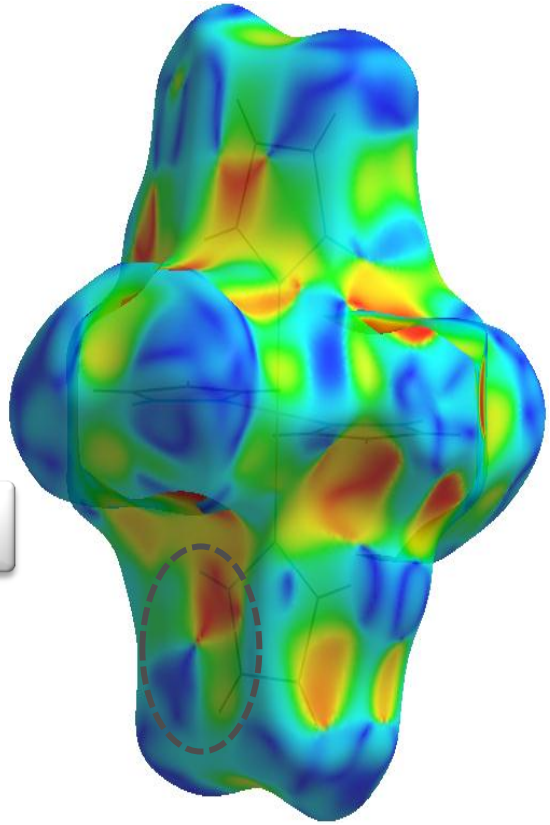
Hirshfeld suraface analysis
C…N/N…C Contacts



N(1)$_{paires\ libres}$…π(–C1)
(3.50 Å)

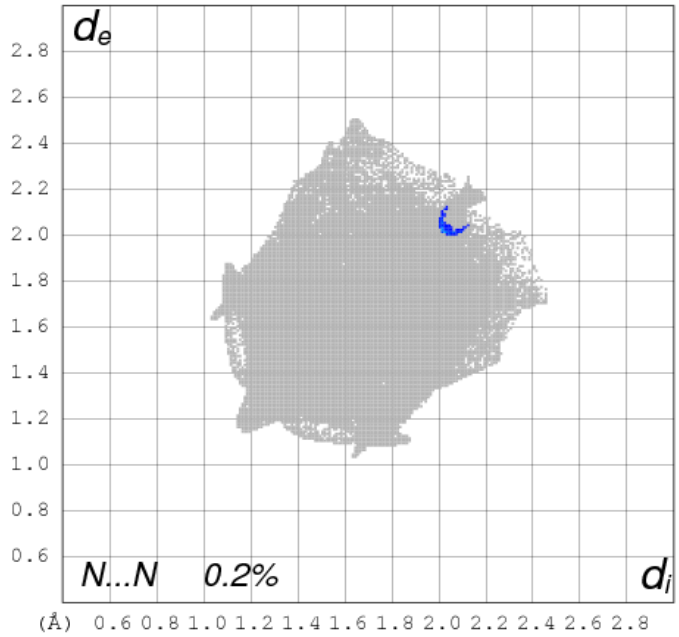
6 Contacts

3 $N_{paires\ libres}$…π



Results and discussion

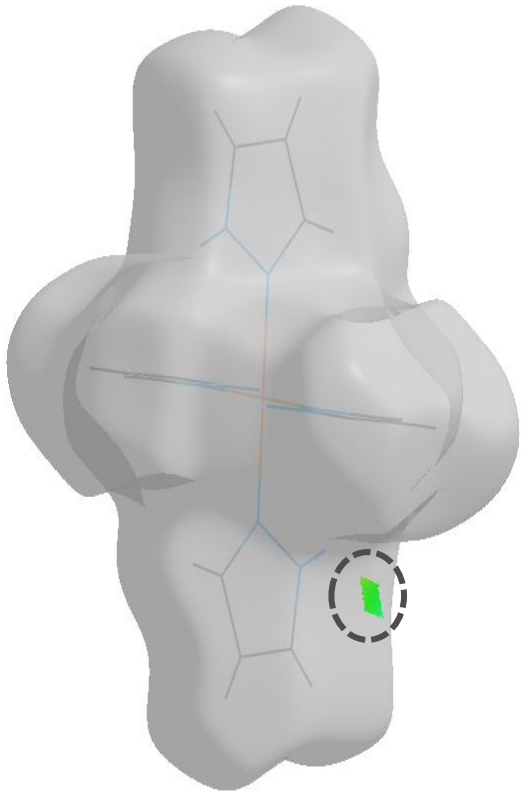
Hirshfeld suraface analysis
N…N Contacts



N(2)$_{paires\ libres}$…N(2)$_{paires\ libres}$
(4.04 Å)

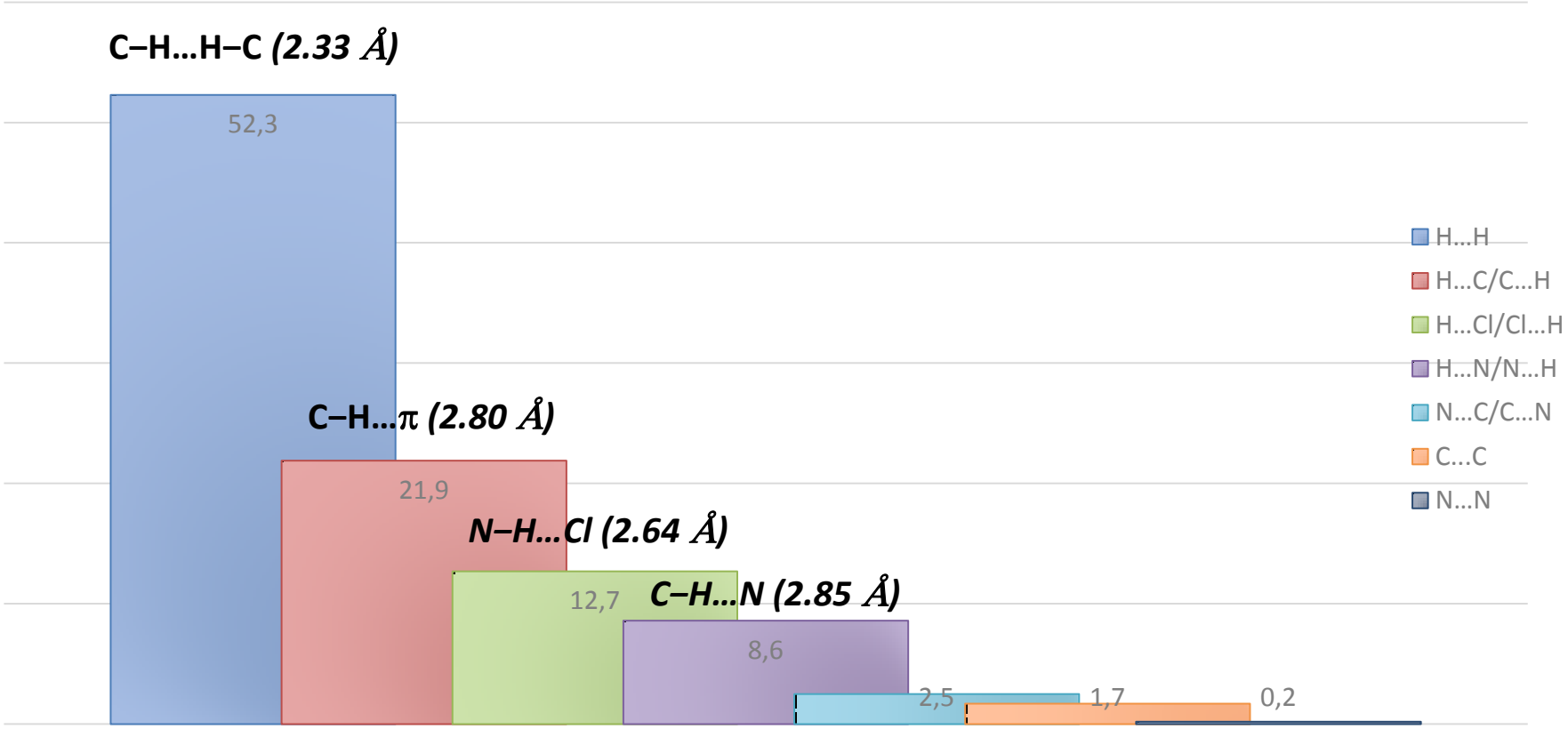
1 Contacts

1 $N_{paires\ libres}$…$N_{paires\ libres}$



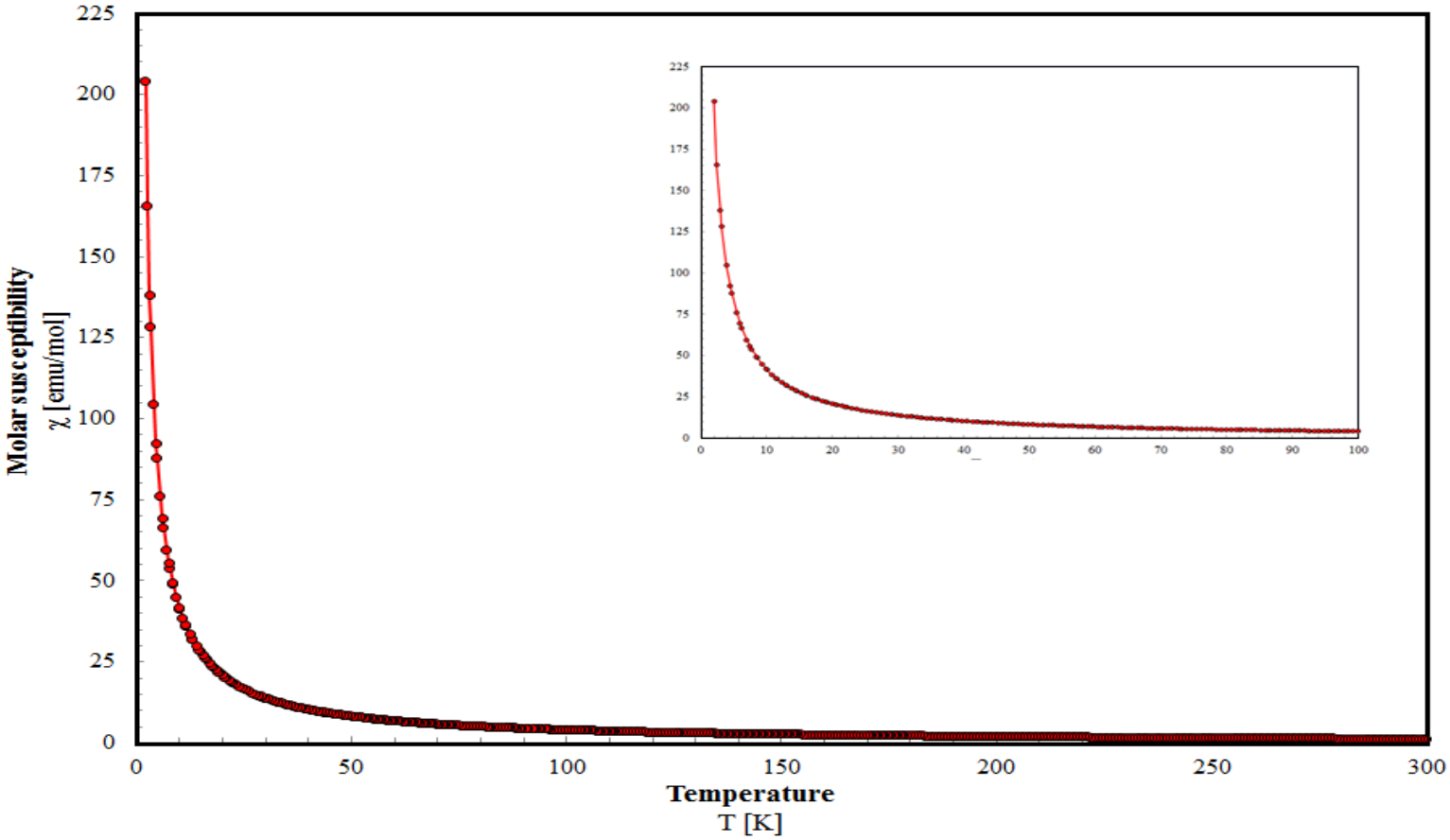
Results and discussion

Hirshfeld suraface analysis



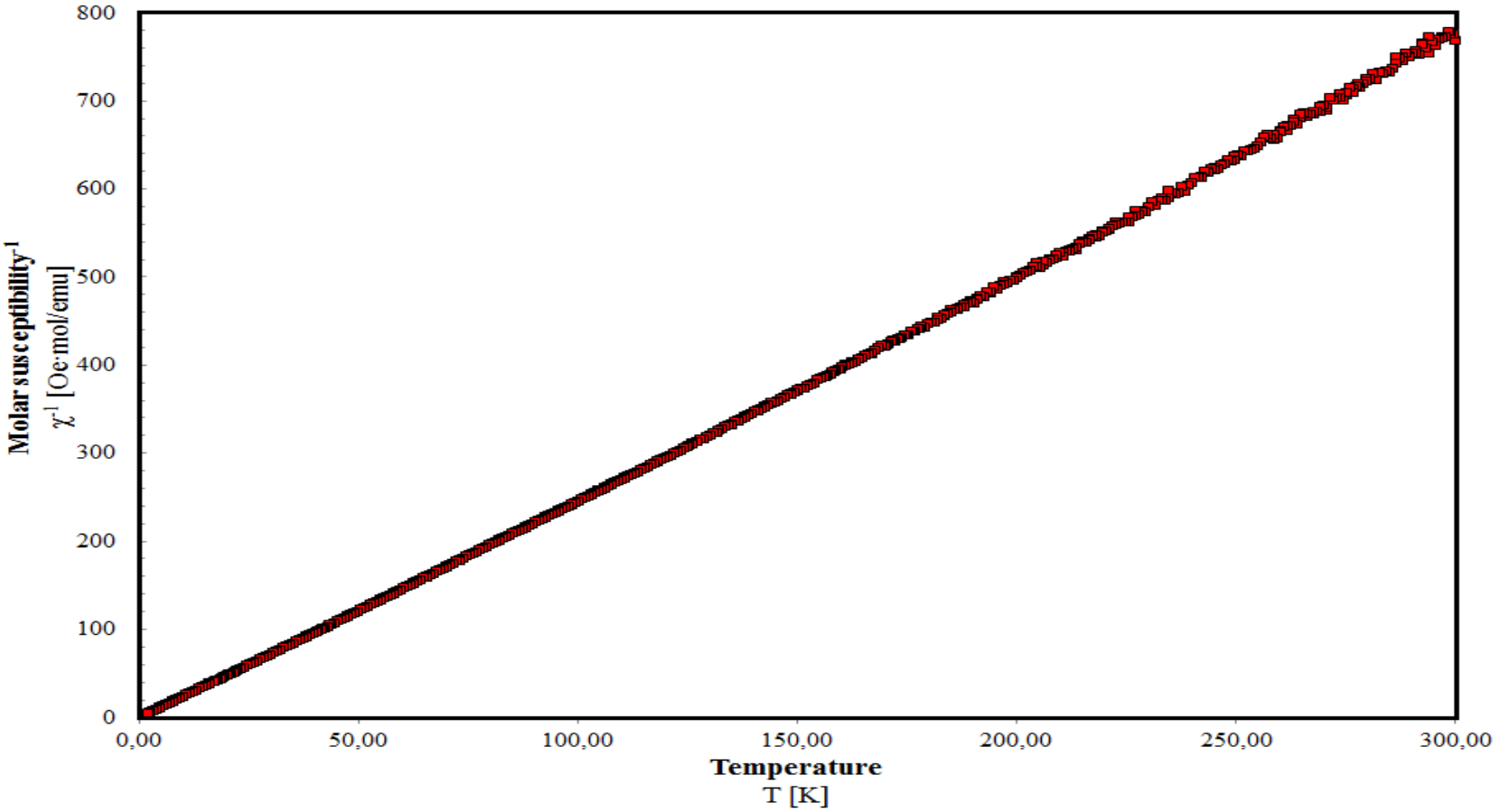
Results and discussion

Magnetic properties



Results and discussion

Magnetic properties



Results and discussion

Magnetic properties

Cation	θ (K)	χ_m (cm^3/mol)	C_m ($cm^3.K/mol$)	$\mu_{eff\ exp}$ (μ_B)	g	J	$\mu_{eff\ cal}$ (μ_B)
Cu(II)	-0.5	$-1{,}19 \times 10^{-4}$	0,423	1.84	2.091	0.494	1.80

Results and discussion

Biological activity

The complex was tested for its in-vitro antibacterial activity against *Staphylococcus aureus* and *Escherichia coli*. Moreover, it was screened against two fungi, namely *Candida specie* and *Aspergillus niger*.

Results and discussion

Biological activity

	(1)	
	C_1 = 10 mg·mL^{-1}	C_2 = 20 mg·mL^{-1}
Staphylococcus aureus	NE	NE
Escherichia coli	NE	NE
Candida specie	NE	08
Aspergillus niger	12	18

Results and discussion

Biological activity

On the basis of the minimum inhibitory concentration (M.I.C) and the diameter of the inhibition zone, the complex (**1**) showed higher fungicidal activity against *Aspergillus niger* (12 mm for C1 = 10 $mg \cdot mL^{-1}$ and 18 mm for C2 = 20 $mg \cdot mL^{-1}$) compared to its inhibition of *Candida specie* (08 mm for C2 = 10 $mg \cdot mL^{-1}$).
However, it has showed no effect on the tested bacteria.

Conclusions

A pyrazole-based copper (II) complex was synthesized and fully characterized using FTIR spectroscopy and single-crystal X-ray diffraction. The *Hirshfeld* surface analysis has showed the presence of diverse unconventional intermolecular interactions, namely N–H…Cl, C–H…Cl, C–H…N, C–H…H–C and N–H…H–C. The magnetic results measured at 2-300K have shown a paramagnetic behavior, which was predicted from the crystal structure displaying a discrete mononuclear complex, with a shortest Cu…Cu distance of 8.172 Å.

By screening the pyrazole complex against *Staphylococcus aureus* and *Escherichia coli*, we have found out that it has no considerable effect for the given concentrations. Nevertheless, it has displayed an interesting activity against the screened fungi, namely *Aspergillus niger* and *Candida specie*, with a higher inhibition of the second specie.

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