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A combined experimental and theoretical study of an oxalato-bridged copper(II) complex : Crystal structure and *Hirshfeld* surface analysis of the non-covalent interactions

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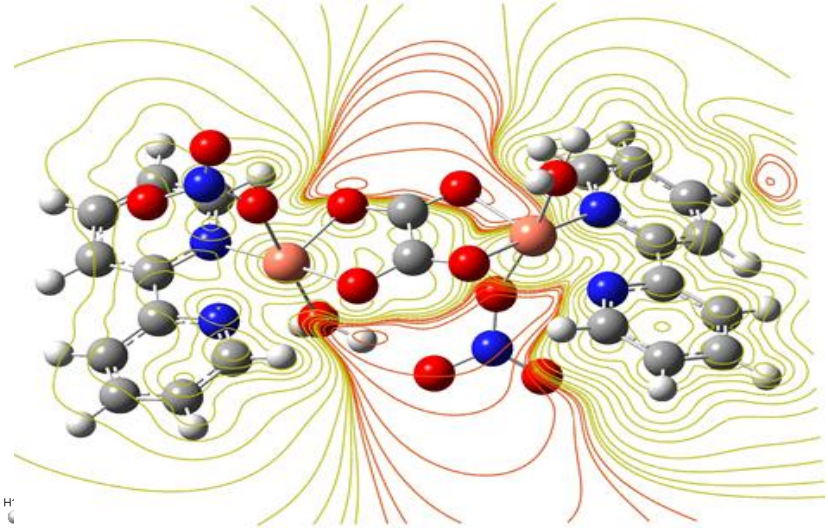
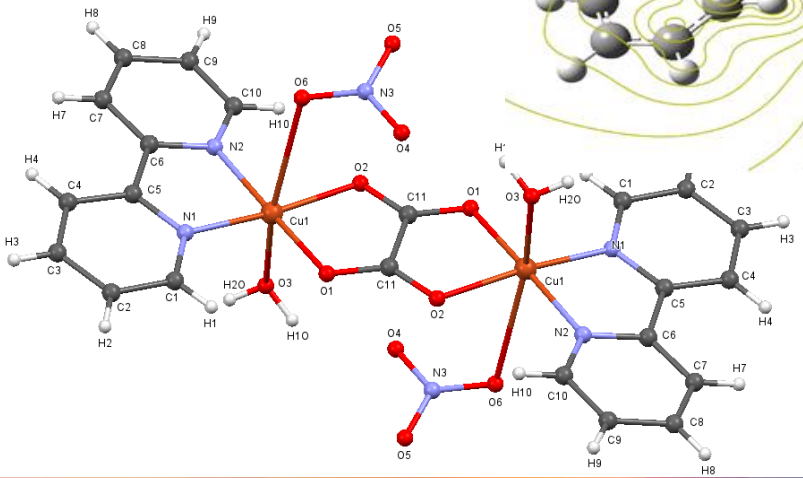
A combined experimental and theoretical study of an oxalato-bridged copper(II) complex : Crystal structure and *Hirshfeld* surface analysis of the non-covalent interactions

Graphical Abstract





Abstract:

A bipyridine-copper complex was synthesized and characterized by single-crystal X-ray diffraction and FT-IR spectroscopy. The structure determination revealed that the studied complex contains centrosymmetric doubly-charged dinuclear oxalato-bridged copper(II) cations, nitrate counter-ions and water molecules. The *Hirshfeld* surface analysis of the complex has shown the presence of moderate O-H…O and C-H…O hydrogen bonds together with non-classical weak C-H…π, π…π, π…*lp*/*lp*…π and *lp*…*lp* intermolecular interactions. Furthermore, the theoretical calculations and structure optimization carried out were found to be in agreement with the experimental geometric parameters. The NMR spectrum was also calculated and the MEP maps examined showing the nucleophilic regions .

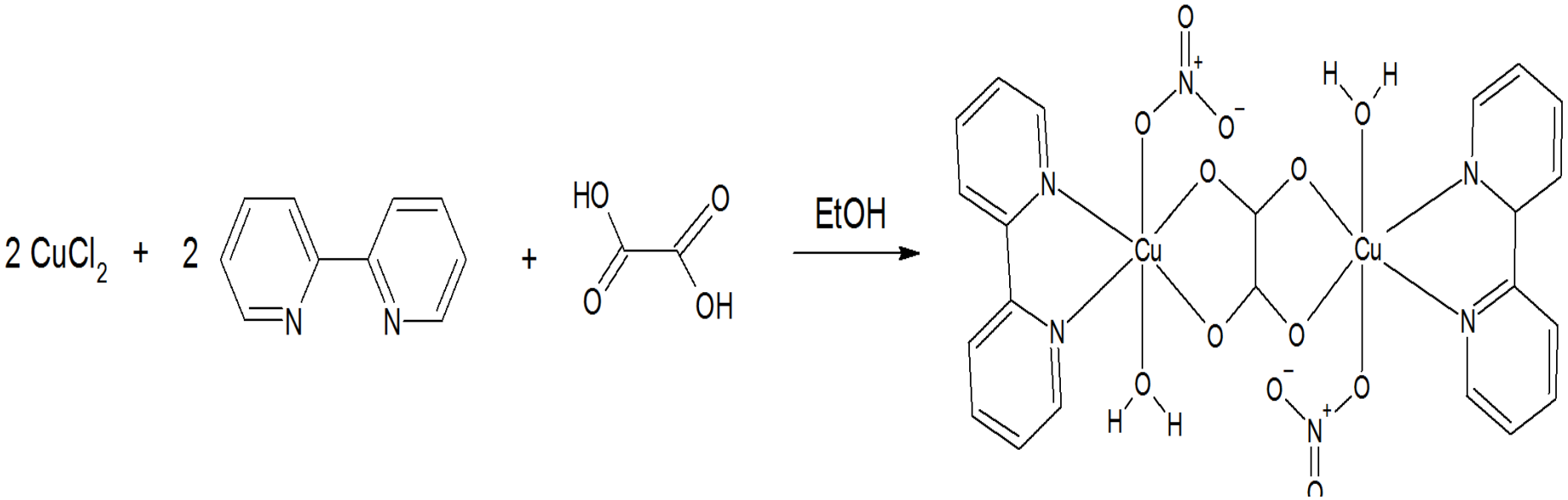
Keywords: Oxalato-bridged complexes, crystal structure, hydrogen bonds, *Hirshfeld* surface analysis, theoretical calculation, MEP.

Introduction

The rich structural diversity of the oxalato-bridged complexes is due to the exceptional versatility of the oxalate ligand. Moreover, the oxalate-bridge can efficiently mediate the exchange interactions between the paramagnetic metal ions, leading to interesting magnetic properties [1-4]. The construction of oxalate-containing homo- and hetero-metallics, which have applications as molecular-based magnetic materials, has enhanced the interest in the oxalato compounds. We will describe herein the *Hirshfeld* surface analysis [5,6] of the intermolecular interactions within our newly published oxalato-bridged copper (II) complex [7]. Moreover, the computational studies [8], accomplished using the HF/LANL2DZ level in gas phase, undertaken on the complex in terms of the optimized structure, the molecular electrostatic potential (MEP) maps and the nuclear magnetic resonance (NMR) will be given.

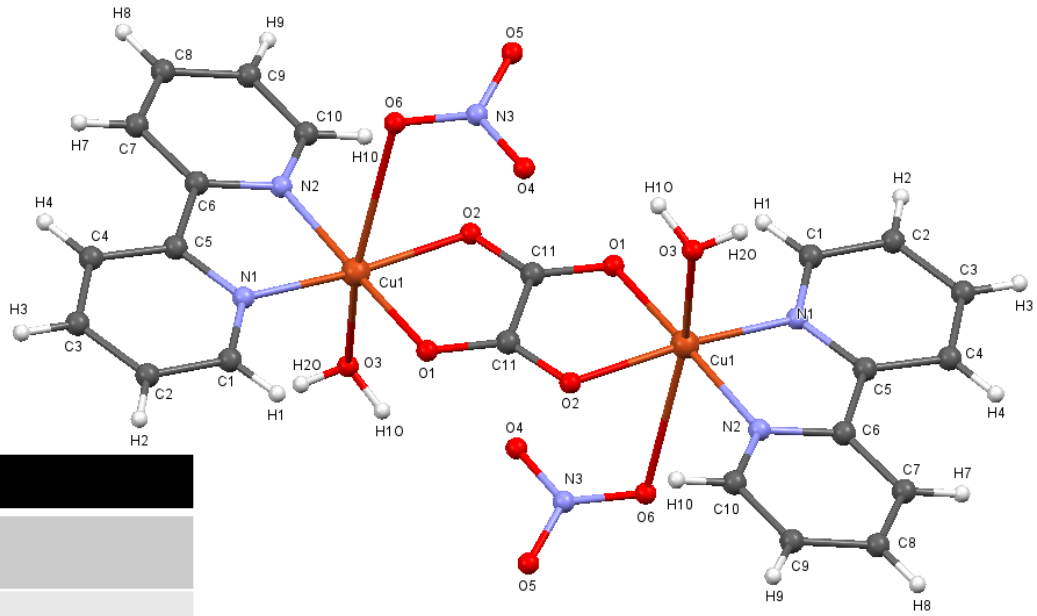
Results and discussion

Synthesis



Results and discussion

Crystal structure



Space Group	$P2_1/n$
a (Å)	7.6587(3)
b (Å)	10.2273(4)
c (Å)	16.1551(6)
β (°)	99.583(4)
$R[F^2 > 2\sigma(F^2)]$	0.0368
$wR(F^2)$	0.0907
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.686, –0.519

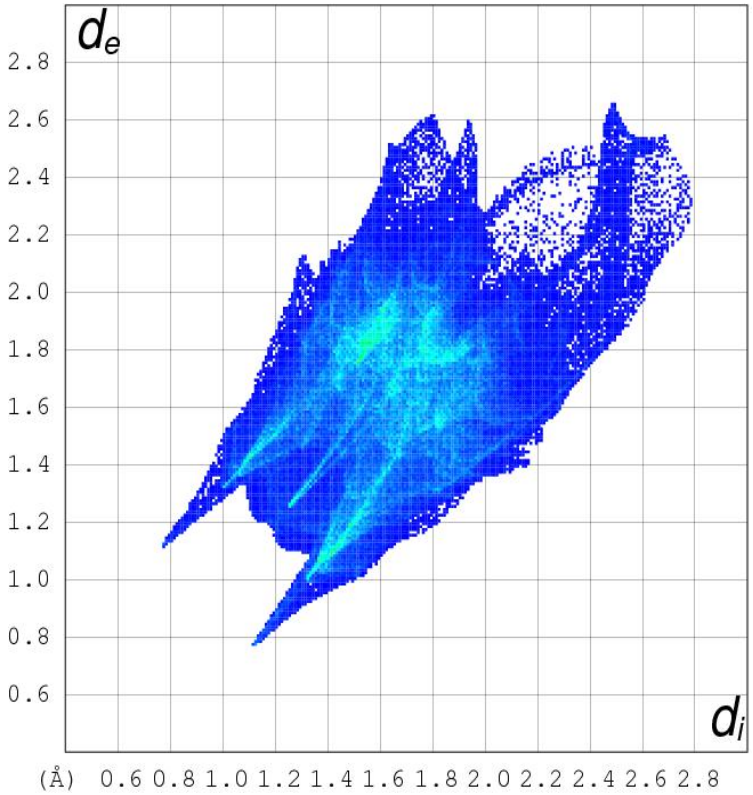
Results and discussion

Hydrogen bonding

D-H…A	D-H	H…A	D…A	D-H…A
Intramolecular interactions				
O3-H1O…O4 (i)	0.86	2.14	2.871(3)	142
C1-H1…O1	0.93	2.58	3.090(3)	115
Intermolecular interactions				
O3-H2O…O5 (ii)	0.81	2.03	2.781(2)	155
C2-H2…O5 (iii)	0.93	2.59	3.508(3)	170
C2-H2…O6 (iii)	0.93	2.51	3.266(3)	139
C4-H4…O4 (iv)	0.93	2.48	3.409(3)	176
C7-H7…O4 (iv)	0.93	2.56	3.489(3)	178
C7-H7…O6 (iv)	0.93	2.42	3.105(3)	131
C9-H9…O5(v)	0.93	2.53	3.230(3)	132
C9-H9…O2(v)	0.93	2.63	3.460(3)	149
C10-H10…O2	0.93	2.65	3.153(3)	115

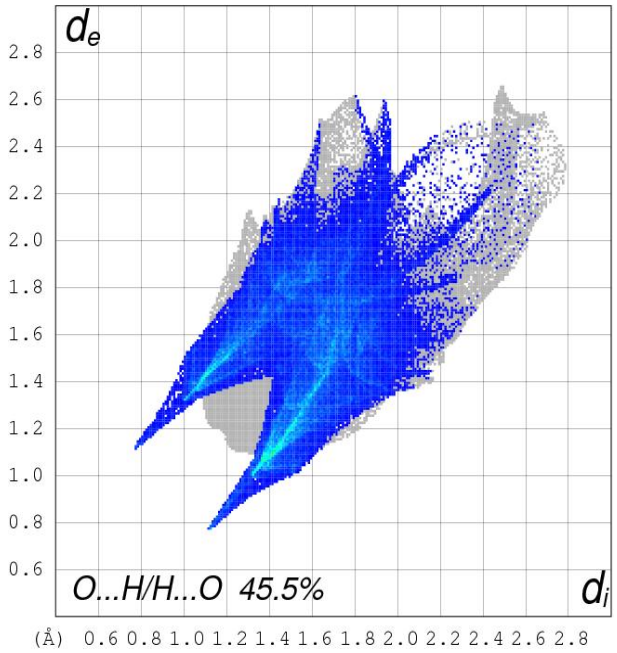
Results and discussion

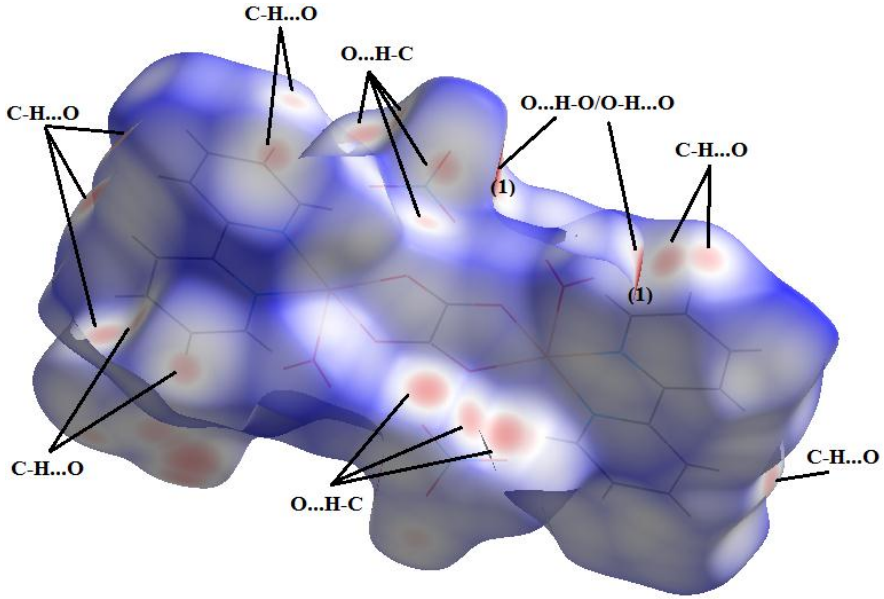
Hirshfeld surface analysis



Results and discussion

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

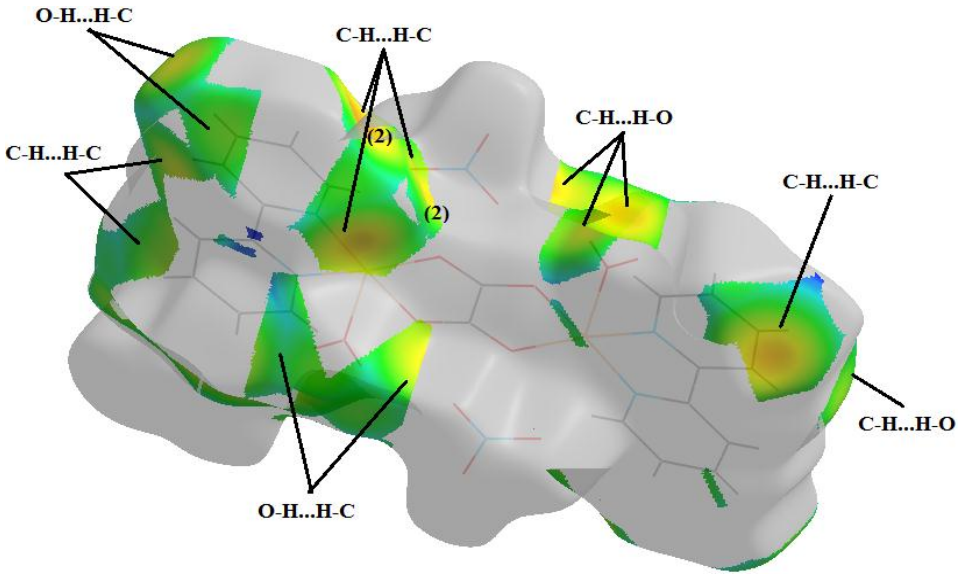


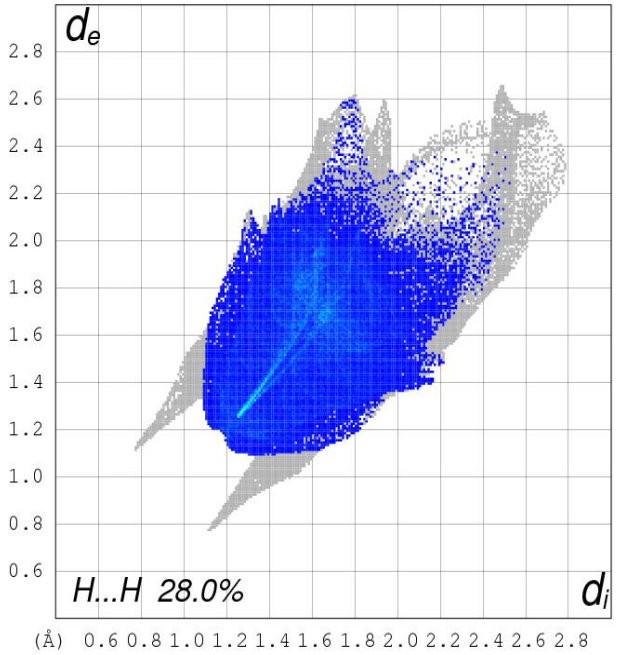


Results and discussion

Hirshfeld surface analysis

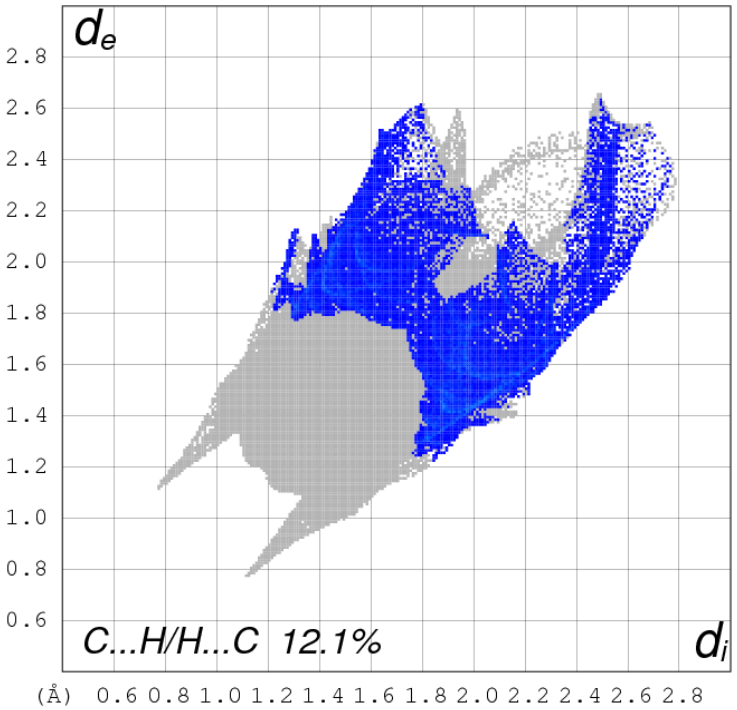
H…H contacts :

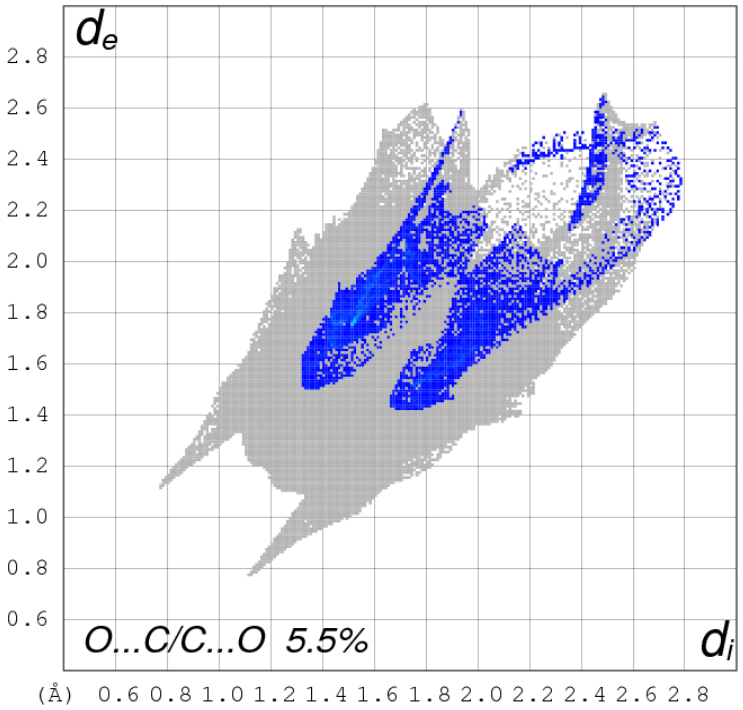




Results and discussion

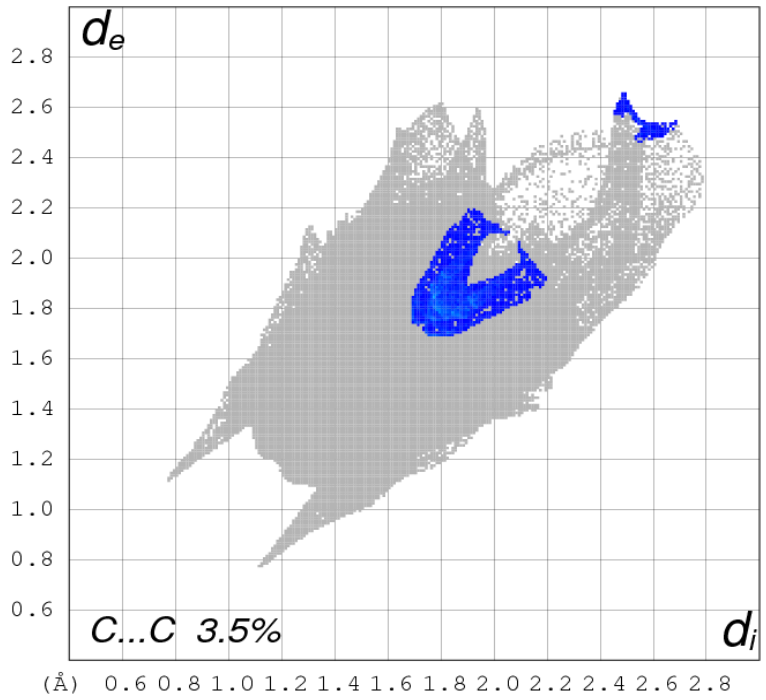
Hirshfeld surface analysis

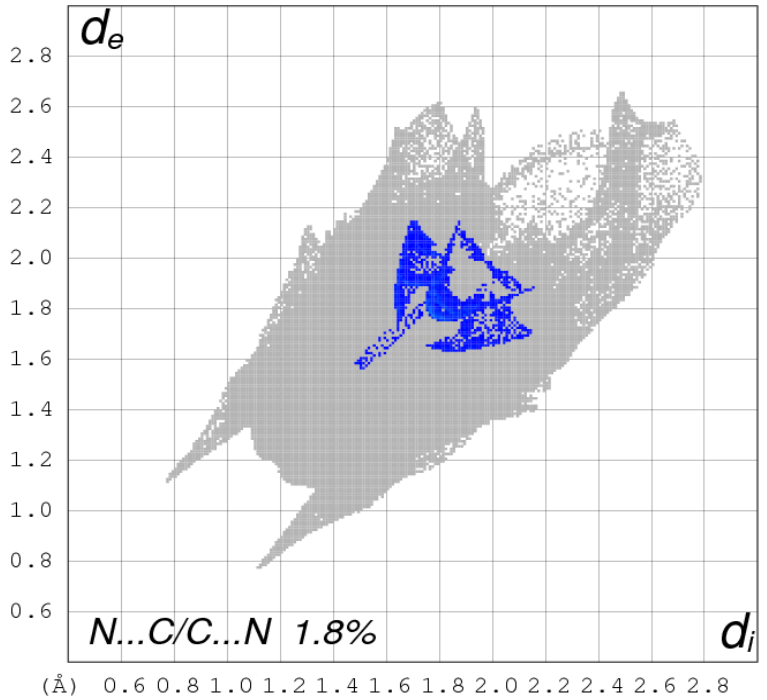




Results and discussion

Hirshfeld surface analysis



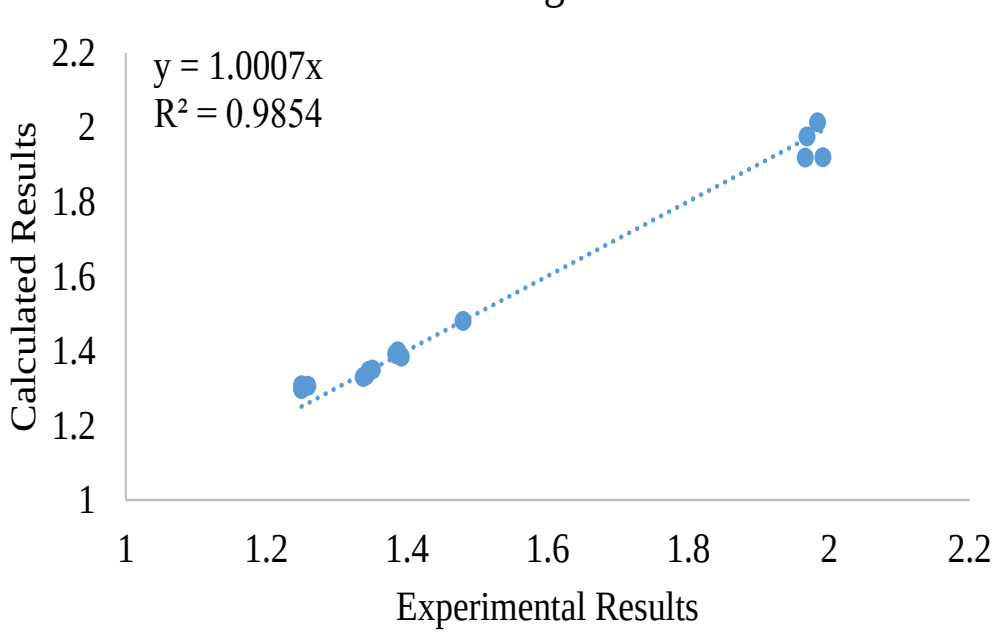


Results and discussion

Quantum calculations

Optimized structure

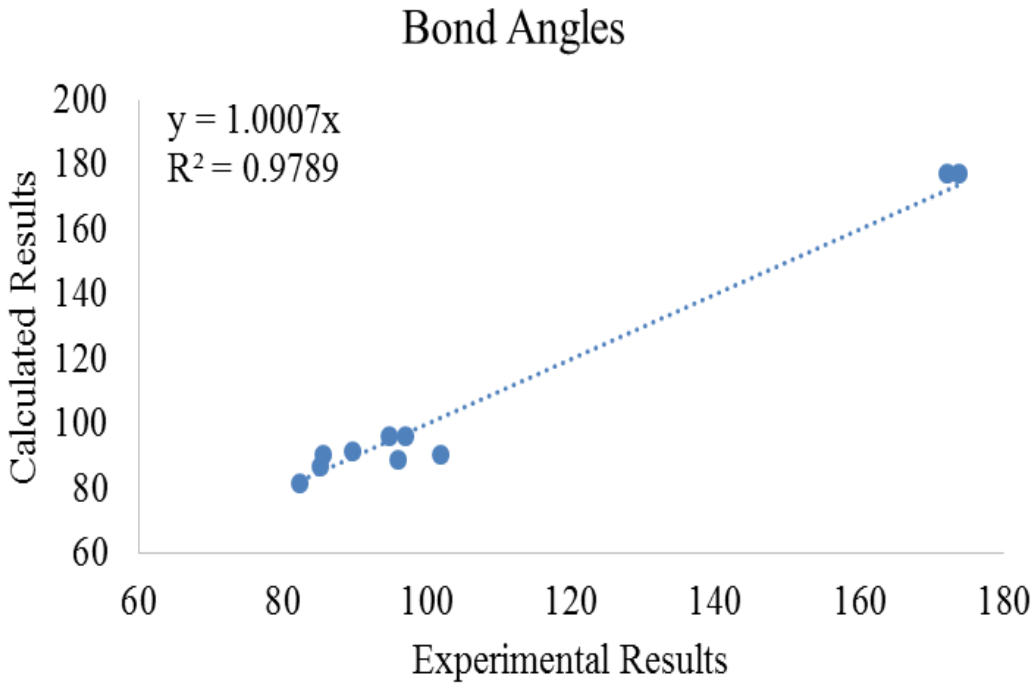
The complex structure was optimized at HF method with LANL2DZ basis set in vacuum.



Results and discussion

Quantum calculations

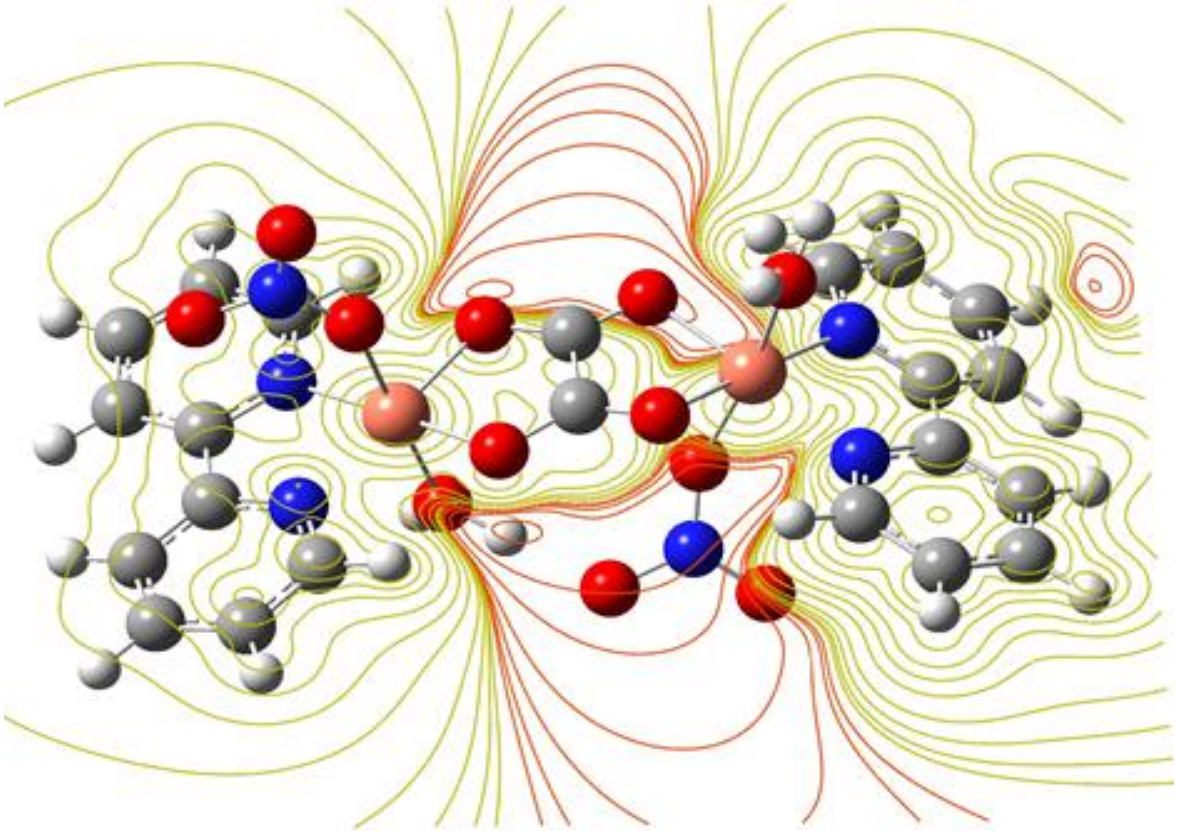
Optimized structure



Results and discussion

Quantum calculations

MEP



Results and discussion

Quantum calculations

NMR spectra

Assignments	^{13}C-NMR	Assignments	^{1}H-NMR
C1	163.38	C1-H1	10.48
C2	130.46	C2-H2	8.17
C3	146.52	C3-H3	8.70
C4	123.86	C4-H4	8.69
C5	167.54	C7-H7	8.75
C6	169.03	C8-H8	8.73
C7	124.26	C9-H9	8.18
C8	146.82	C10-H10	10.87
C9	129.82	O3-H1O	1.50
C10	164.46	O3-H2O	1.87
C11	196.95		

Conclusions

The *Hirshfeld* surface analysis of a newly synthesized oxalato-bridged copper(II) complex has shown that the presence of weak C-H…π, π…π, π…*lp*/*lp*…π and *lp* …*lp* intermolecular interactions, in addition to the strong O-H…O, N-H…O and C-H…O hydrogen bonds. The quantum chemical calculations performed using HF/LANL2DZ levels indicated a good agreement between the calculated and experimental geometric structural parameters. Moreover, the ^{1}H, ^{13}C-NMR spectra, the MEP maps and the MEP contours were calculated, examined in detail and the nucleophilic regions determined.

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