

## Synthesis, XRD, DFT-optimization, MEP and Hirshfeld surface analysis of di- $\mu$ -Chloro-bis[chloro(1,10-phenanthroline)Cd(II)]dimer

Sameer Amereih<sup>1</sup>, Anas Al Ali<sup>2</sup>, Abdelkader Zarrouk<sup>3</sup>, Ahmed Chetouni<sup>4</sup>, Karthik Kumara<sup>5</sup>, Neartur K. Lokanath<sup>5</sup>, Ismail Warad<sup>2,\*</sup>

<sup>1</sup>Department of Chemistry, Science College, Palestine Technical University, P.O. Box 7, Tulkarm, Palestine

<sup>2</sup>Department of Chemistry, An-Najah National University P.O. Box 7, Nablus, Palestine Laboratory of Materials,

<sup>3</sup>Nanotechnology and Environment, Mohammed V University, Faculty of Science, 4Av. Ibn Battuta, B.P. 1014 Rabat, Morocco

<sup>4</sup>Laboratoire de Chimie Analytique Appliquée, Matériaux et Environnement (LC2AME), Faculté des Sciences, Université Mohamed I, 60 000 Oujda, Morocco

<sup>5</sup>Department of Studies in Physics, University of Mysore, Manasagangotri, Mysuru, 570 006, India

### Abstract

Cadmium(II) dimer complex of type  $[\text{Cd}_2(\text{phen})_2\text{Cl}_4]$  was made available in a high yield, the structure of the dimer was solved by XRD then optimized via density functional theory (DFT) and Hirshfeld computed methods. The structure parameters like: angles and bonds lengths were compared to their DFT-relatives, Hirshfeld surface analysis (HAS), molecular electrostatic potential (MEP) and Mulliken charge populations were also matched to the XRD-packing collected result. The dimer was crystallized in the Triclinic/P-1 system with  $Z = 4$ . The two Cd(II) centers in the dimer found to be with a distorted square-pyramidal geometry. Crystallographic data for desired dimer was deposited to the Cambridge Crystallographic Center under CCDC No. 1911235.

\* Corresponding Author:

Tel.: +972-9234-5982

E-mail: [warad@najah.edu](mailto:warad@najah.edu)

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## 1. Introduction

1,10-Phenanthrolines as bidentate N-ligands are well-known metal ions coordinators [1-6]. Its complexing ability was used to establish metalloenzymes biomimetic for supramolecules self-assembling processes[4]. The M/phenDNA-complex base pairs binding ability were currently develops to be used as chemotherapy agents [7]. Cd(II) is not common used as in metalloenzymes and metalloproteins ion like Zn(II) for example. For long Cd(II) was thought as a highly toxic ion and was often correlated with lead and mercury and as harmful biological ions [5-11]. Currently, interest in the metal ionscomplexes coordination chemistry was increased due to their biological recognition role [9], and structural rich materials [11-16].The metalscoordination behaviors have played a critical role in developing of inorganic material and enhancing their biologically activities [17, 18]. The presence of nitrogen, sulfur, phosphorus and oxygen donors in such complexes reflects high anticancer and antibacterial activities [19]. 1,10-Phen and its derivative can coordinate Cd(II) to form*viabis*-phen dimer or mono-phen simple complexes [13-16]. Cd(II)/phen complexes were broadly reported as bioactivities hybrid material like, antibacterial, DNA binding and antitumor activities [6], Cd(II) ions complexes enhance their anticancer activities since it possessed via low cytotoxic behaviors [20]. Previously, we reported two newCd(II) neutral dimers of  $[Cd_2(dmdphphen)X_4]$  formula was synthesized and characterized by different spectroscopic methods[1-2].In this work we have prepared the  $Cd_2(dmdphphen)Cl_4$  dimer, the structure of the desired dimer was proved by XRD and optimized *via* density functional theory (DFT) and Hirschfield surface analysis (HSA) methods.

## 2. Methodology

### 2.1. Chemicals

$CdCl_2 \cdot 2.5H_2O$  and 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline ligand, were purchased from Fluka.

### 2.2. Crystallography

A colorless block single suitable crystal of D  $0.22 \times 0.25 \times 0.26$  mm of the desired dimer was selected for the XRD-diffraction studies. The X-ray data was performed on a Bruker Proteum2 CCD diffractometer equipped with an X-ray generator operating at 10 mA and 45 kV, using Cu- $K_\alpha$  radiation source of wavelength  $1.54178 \text{ \AA}$  [21-22].

### 2.3. Theoretical calculations

The theoretical calculations in this work are described in previous publications [23].The structure optimized and other physical calculations of the dimer were performed *via* DFT/B3LYP/6-31+G(2d,p) using Gaussian 09 [24] and HAS calculations were performed *via* CRYSTAL EXPLORER 3.1 program[25].

## 3. Results and discussion

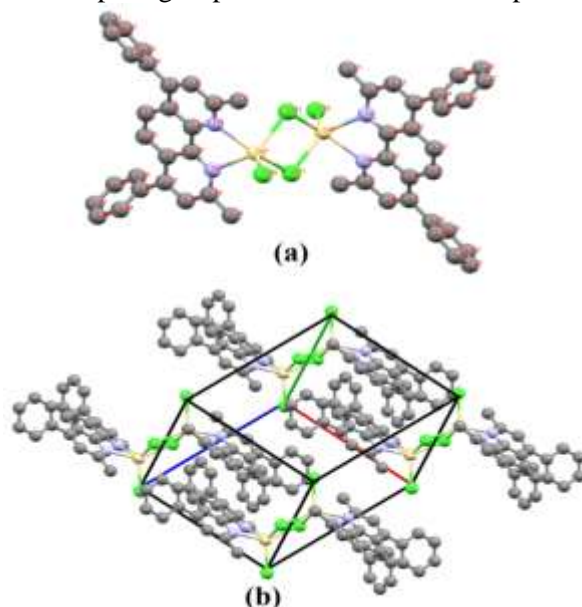
### 3.1. Synthesis of the desired dimer

Treating of phen with  $CdCl_2$  hydrated salt in  $CH_2Cl_2/EtOH$  solvents revealed the formation of  $[CdCl_2(phen)]_2$  dimer in good yield, as seen in Scheme 1. The dimer was XRD characterized and DFT-optimized. Moreover, the conductivity and the solubility reflected the dimer as non-electrolytic complex in its nature.

**Scheme 1.** Dimer synthesis.

### 3.2. X-Ray Crystal structure

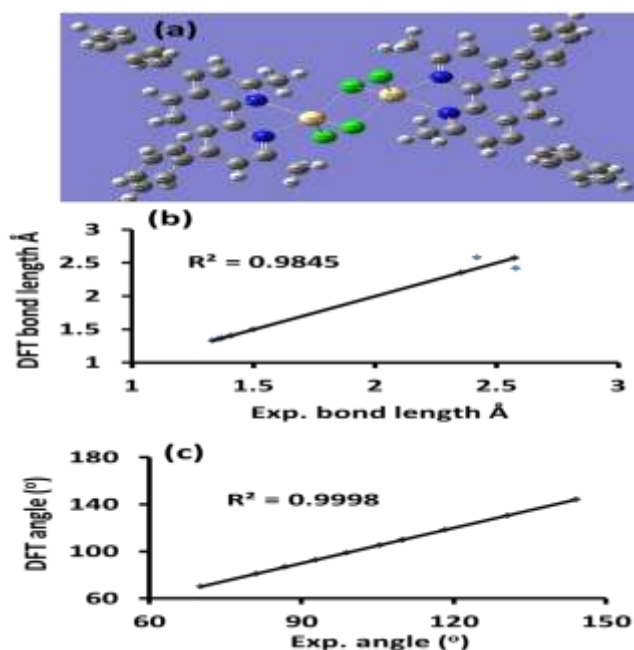
The structure of the desired dimer (Fig. 1a) consists with  $[\text{Cd}_2\text{Cl}_4(\text{dmdphen})_2]$  formation, where 2Cl atoms form bridge to Cd(II) center. The 2Cl atoms and the bidentate chelating phen ligands coordinated neutrally the center. The coordination mode around both Cd(II) centers is slightly distorted square-pyramidal geometry. The dimer was crystallized with triclinic system and *P-1* space group and *Z*= 4 as seen in the packing figure (Fig. 1b).



**Fig.1.** (a)ORTEP and (b) packing system of the desired dimer.

### 3.3. Structure optimizations

The structure of the desired dimer was subjected to B3LYP/6-311G (d,p) optimization (Fig.2a). The structural parameters such as angles and bond lengths were matched to their XRD-experimental relatives. A high degree of matching between theoretical and calculated bond length with 0.985 correlation coefficient was collected as in Fig.2b, and Table 1. Similarly, 0.999 correlation coefficient was recorded by comparing experimental/calculated angles (Fig.2c, and Table 1).



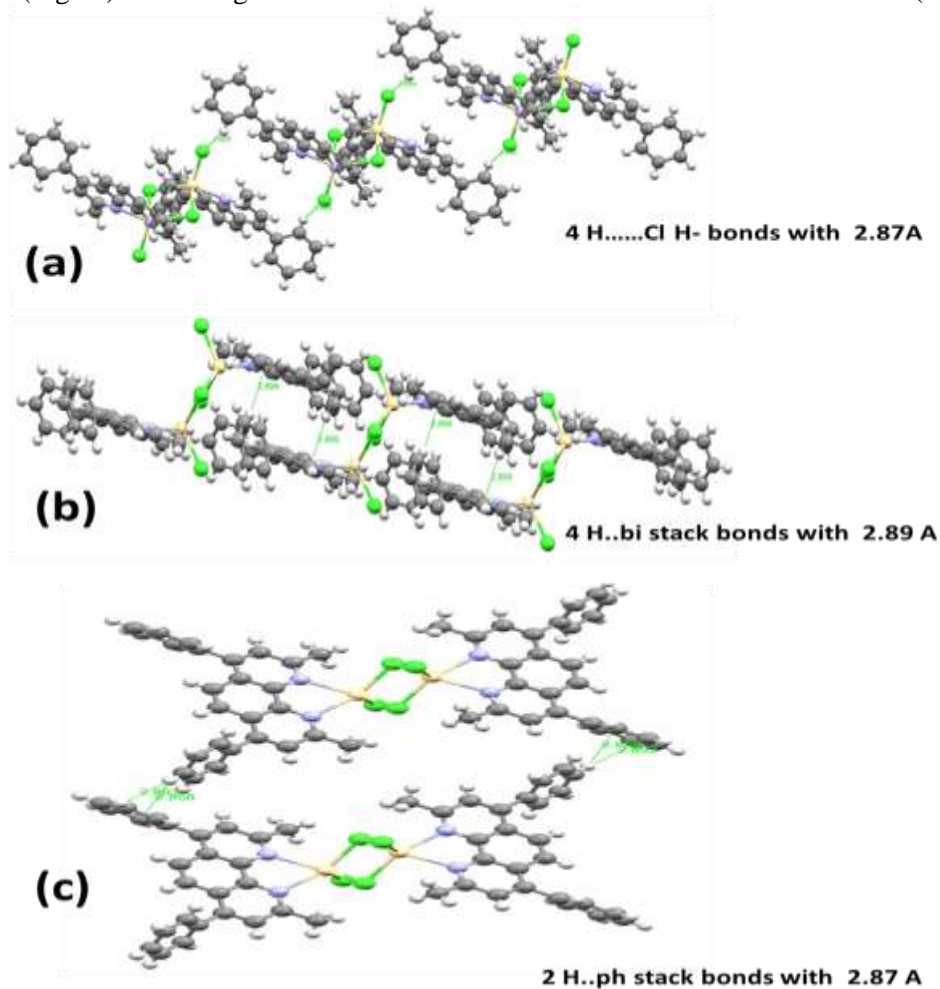
**Fig.2.** (a) Dimer optimized structure B3LYP/6-311G(d), (b) DFT/XRD bond lengths graphical correlation, and (c) DFT/XRD angles graphical correlation.

**Table 1.** Selected XRD/DFT angles ( $^{\circ}$ ) and bond lengths ( $\text{\AA}$ ).

Bond No.	Bonds	Exp. XRD	DFT	Angles No.	Angles ( $^{\circ}$ )	Exp. XRD	DFT
1	Cd1 Cl31	2.578	2.4187	1	Cl31 Cd1 N2	144.1	144.1
2	Cd1 N2	2.354	2.354	2	Cl31 Cd1 N3	86.74	86.74
3	Cd1 N3	2.354	2.3541	3	Cl31 Cd1 Cl30	118.33	118.33
4	Cd1 Cl30	2.419	2.578	4	Cl31 Cd1 Cl31	81.12	81.12
5	Cd1 Cl31	2.573	2.5728	5	N2 Cd1 N3	70.1	70.13
6	Cl31 Cd1	2.573	2.5728	6	N2 Cd1 Cl30	109.83	109.83
7	C15 C14	1.5	1.4995	7	N2 Cd1 Cl31	92.72	92.72
8	N2 C16	1.359	1.3594	8	N3 Cd1 Cl30	105.4	105.4
9	N2 C14	1.333	1.3332	9	N3 Cd1 Cl31	130.61	130.61
10	C6 C7	1.37	1.3705	10	Cl30 Cd1 Cl31	110.12	110.12

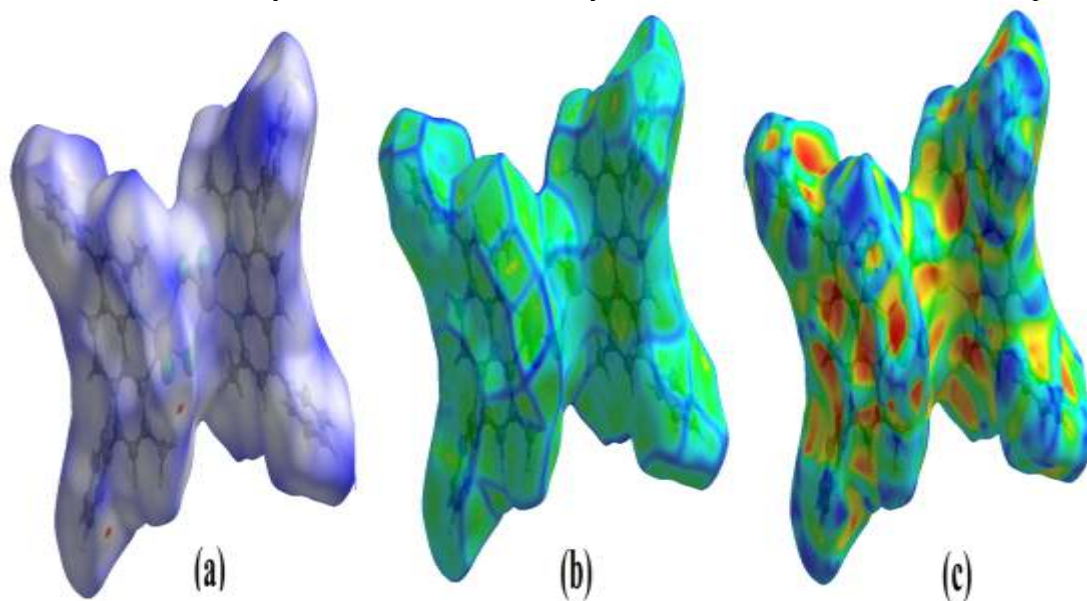
### 3.4. Crystal interactions, HAS and 2D Fingerprint (FP)

Many shorter interactions ( $<3 \text{ \AA}$ ) were recorded in the crystal lattice of solved XRD experimental structure, since three heteroatoms 2Cd, 6Cl, 4N and several polar H atoms detected in the dimer formula, therefore, 4 shorter H-bonds as  $\text{H}\cdots\text{Cl} = 2.871 \text{ \AA}$  connected molecule with its neighbors strongly as illustrated in Fig.3a. Moreover, 4  $\text{H}\cdots\text{ph}$  stacked bonds with  $2.898 \text{ \AA}$  (Fig.3b) and 2 longer  $\text{H}\cdots\pi$ -bonds were detected with  $\text{C}=\text{C}\cdots\text{H} = 2.879 \text{ \AA}$  (Fig.3c).

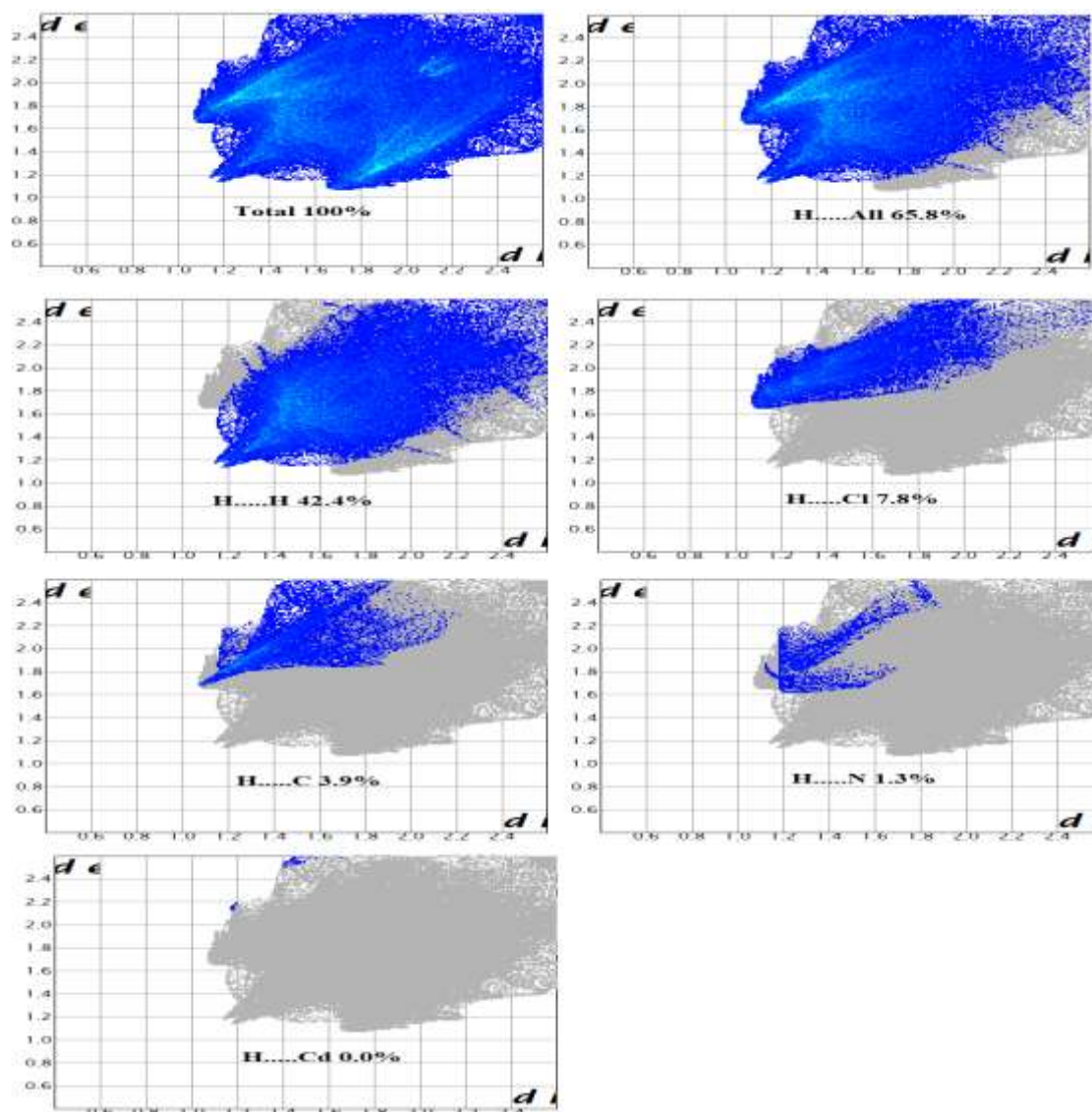
**Fig.3.** Molecular interactions bonds types and lengths.



In HAS (Fig.4), 10 big red spots were recorded close to the Cl and N atoms as seen in the  $d_{\text{norm}}$  surface (Fig.4a), such sport reflected the formation of many short interaction in the crystal lattice of the dimer as see in the packing result.



**Fig.4.** (a)  $d_{\text{norm}}$ , (b) curvedness and (c) shape index mapped structures.

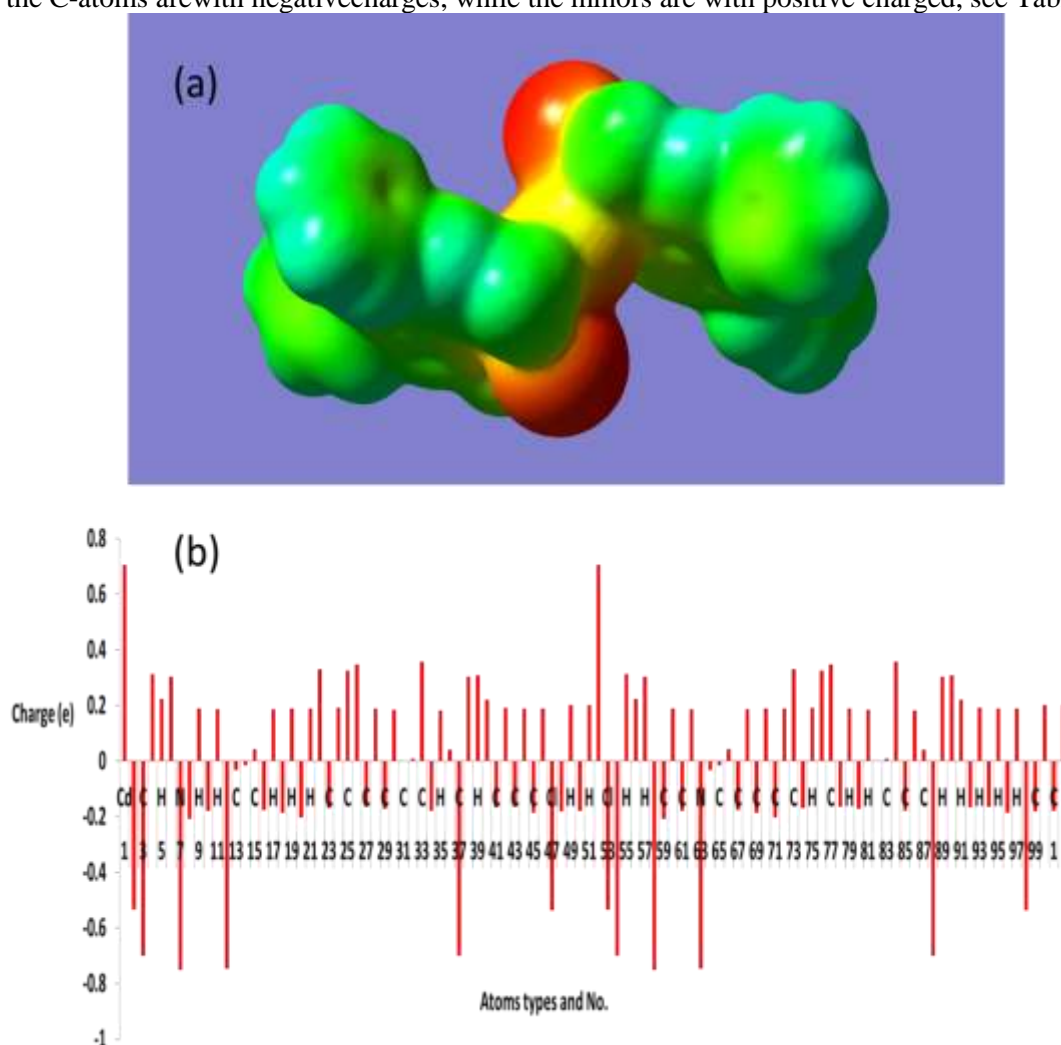


**Fig.5.**Inside...outside atoms 2D-FP ratios.

By subjecting the dimer to 2D-Fingerprint analysis as seen in Fig.5, the plot reflected the H...H as the highest interactions, meanwhile the H...Cd as the lowest interactions presence ratios, moreover, the presence ratios for the whole interactions ratios were illustrated as the following. H...H (42.8%) > H...C (7.8%) > H...S (6.9%) > H...Cl (3.9%) > H...N (1.7%) with H...overall connections (65.8%), as depicted in Fig. 5.

### 3.5.B3LYP/6311G(d,P) MEP and Mulliken charge distribution investigations

The MEP analysis and Mulliken indicates that the intermolecular bonding are reasonable, since all the corresponding H-donor atoms are with positive charge and nearby negatively charged nitrogen and chloride atoms. The MEP diagram was served to evaluate the nucleophilic reactive sites for electrophilic one, and for figures out the molecular interactions [26]. The MEP/B3LYP map analysis of the desired dimer revealed an electrophilic/nucleophilic functional groups reflected by their color as the following [red (highest)>orange>yellow>green>blue (lowest)] as seen in Fig.6a. The MEP proved the presence of both e-poor/e-rich positions in the complex, for example, intensity red color reflected the Cl atoms as good nucleophile sites, the yellow color around the N and most of C atoms also reflected as nucleophile sites, on the other hand, the Cd and most of the H atoms were reflected with blue color showing a electrophilic sites [27]. Since MEP reflected the presence of both blue and red colors sites in the dimer structure it is, therefore consistent strongly with Mulliken charges result illustrated in Fig.6b. Fig.6b. and Table 2 show Mulliken population analysis of each atom. As predicted, the N and Cl-atoms are the highest electronegative atom, respectively, all the H-atoms are electropositive which enhanced for example the H...Cl hydrogen bonds formation, On the other hand, most of the C-atoms are with negative charges, while the minors are with positive charged, see Table 2.



**Fig.6.**B3LYP/6311G(d,P) (a) MEP and (b) Mulliken atomic charges.

**Table 2.** Mulliken atomic charges of all atoms belong to the desired dimer.

Atom No.	Atoms	Charge (e)	Atom No.	Atoms	Charge (e)
1	Cd	0.706853	52	Cd	0.70683
2	Cl	-0.53431	53	Cl	-0.53431
3	C	-0.69953	54	C	-0.69951
4	H	0.31285	55	H	0.312848
5	H	0.224428	56	H	0.224419
6	H	0.305304	57	H	0.3053
7	N	-0.75051	58	N	-0.75049
8	C	-0.20704	59	C	-0.20704
9	H	0.188571	60	H	0.188566
10	C	-0.17841	61	C	-0.17841
11	H	0.187559	62	H	0.187568
12	N	-0.74478	63	N	-0.74479
13	C	-0.03121	64	C	-0.03119
14	C	-0.01547	65	C	-0.01546
15	C	0.044306	66	C	0.044308
16	C	-0.17629	67	C	-0.17629
17	H	0.188242	68	H	0.188223
18	C	-0.18509	69	C	-0.1851
19	H	0.189977	70	H	0.189985
20	C	-0.20323	71	C	-0.20325
21	H	0.190286	72	H	0.190285
22	C	0.329812	73	C	0.329837
23	C	-0.16785	74	C	-0.16782
24	H	0.191195	75	H	0.19119
25	C	0.326212	76	C	0.326194
26	C	0.34734	77	C	0.347326
27	C	-0.16356	78	C	-0.16358
28	H	0.189974	79	H	0.189992
29	C	-0.17047	80	C	-0.17046
30	H	0.183728	81	H	0.183717
31	C	0.003029	82	C	0.003028
32	C	0.009406	83	C	0.009389
33	C	0.35842	84	C	0.358426
34	C	-0.17875	85	C	-0.17875
35	H	0.183366	86	H	0.183357
36	C	0.041591	87	C	0.04159
37	C	-0.70054	88	C	-0.70054
38	H	0.304554	89	H	0.304554
39	H	0.30987	90	H	0.309865
40	H	0.222164	91	H	0.222174
41	C	-0.16477	92	C	-0.16477
42	H	0.191811	93	H	0.191815
43	C	-0.16375	94	C	-0.16374
44	H	0.188993	95	H	0.188992
45	C	-0.18518	96	C	-0.18519
46	H	0.189911	97	H	0.189913
47	Cl	-0.53547	98	Cl	-0.53546
48	C	-0.17942	99	C	-0.17944
49	H	0.202061	100	H	0.202053
50	C	-0.17879	101	C	-0.17876
51	H	0.202599	102	H	0.202599

#### 4.CONCLUSION

In this work, novel  $\text{Cd}_2(\text{phen})_2\text{Cl}_4$  dimer was prepared in a very good yield via efficient and simple synthetic way. The dimer was characterized by XRD and structurally computed via HAS and DFT. The XRD reflected the Cd(II) ions dimer as triclinic/P-1 system with slightly-distorted square-pyramidal centered. The computed angles and bonds lengths reflected an excellent matching with the experimental XRD one. The HAS and 2D-FP calculations supported the experimental-packing result, where three difference short contacts were discovered in the crystal lattice of the desired dimer, MEP and Mulliken charge population reflected the presence of both nucleophilic and electrophilic positions in the backbone of the dimer which strongly supported the formation of intermolecular bonds detected by XRD result.

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