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Synthesis, crystal structure, Hirshfeld surface analysis and characterization of a new Cd(II) complex with the 4,4'-dimethyl-2,2'-dipyridine monodentate ligand

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Abstract

Synthesis, crystal structure and spectroscopic characterization of the new Cd(II) complex with the bidentate ligand 4,4'-dimethyl-2,2'-dipyridine (DMDPy), [CdI₂(DMDPy)₂], is reported. The cadmium cation is hexa-coordinated in a distorted octahedral configuration by four nitrogen atoms of two DMDPy ligands and two iodide anions. In the structural arrangement of the title compound, the different chemical entities are arranged in planes around $z = n \pm 1/4$. Intermolecular interactions were investigated by Hirshfeld surface and contact enrichment tools. Mulliken charge distribution, molecular electrostatic potential (MEP) maps and HOMO/LUMO energy gaps were computed. Infrared spectroscopy was used to verify the functional groups present in the compound and to study their vibrational behavior in the crystalline state.

Keywords: Cadmium (II) complex • X-ray structure • Hirshfeld surface • contact enrichment ratio • DFT calculations.

Introduction

Cadmium (II) complexes have attracted considerable attention during the past decade thanks to their functional properties such as luminescent potential [1], urease inhibitory activity [2], corrosion inhibitory effect [3], photocatalytic activity [4], etc. Cadmium (II) cation with d^{10} configuration can adopt many coordination geometries, which may include tetrahedral, trigonal bipyramidal, square pyramidal and octahedral and are particularly useful for the development of coordination frameworks [5]. When it comes to organic ligands, 2,2'-bipyridines have enjoyed considerable success as ligands in metal complexes, because of their ability to coordinate a spread of metal ions in several oxidation states [6]. Pyridine rings present in bipyridines increase the electron delocalization and conformational rigidity upon coordination to the metal ion, and therefore improve π -conjugated systems and tune the optical, electrochemical, catalytic and biological properties of the complexes [7].

In this paper, we report the synthesis, Hirshfeld surface analysis and physicochemical characterization of a new Cd(II) complex with the bidentate ligand 4,4'-dimethyl-2,2'-dipyridine $[\text{CdI}_2(\text{DMDPy})_2]$.

Experimental

Chemical preparation

The synthesis of the $[\text{CdI}_2(\text{DMDPy})_2]$ complex was carried out by addition of a solution of 4,4'-dimethyl-2,2'-dipyridine (0.4 mmol) in ethanol (20 mL) to a solution of CdI_2 (0.2 mmol) in water (5 mL). After stirring for 45 min, the mixture was filtered and the resultant solution was allowed to evaporate at room temperature. Transparent prismatic single crystals of the title compound, which remained stable under normal conditions of temperature and humidity, were

isolated after several days and subjected to X-ray diffraction analysis (yield 69%). Anal. Calc.: C, 19.46; H, 2.26; N, 15.90. Found: C, 19.15; H, 2.57; N, 15.69.

X-ray single crystal structural analysis

A light green crystal of the material with dimensions $0.067 \times 0.079 \times 0.087$ mm³ was selected and mounted on a glass fiber. Diffraction data were obtained at 100 K on a Bruker D8 Venture diffractometer equipped with a Photon III CMOS area detector and with a Mo-K α radiation ($\lambda = 0.71073$ Å) X-ray microfocus source. The X-ray intensities were corrected using multi-scan method applied by SADABS [8]. The crystal structure was solved by use of the ShelXT program using intrinsic phasing method and refined by full-matrix least-square techniques on F^2 using the ShelXL-2014 program [9, 10]. All non-hydrogen atoms were refined anisotropically. The positions of all hydrogen atoms were introduced at ideal position and refined as riding atoms with isotropic displacement parameters ADPs ($U_{\text{isoH}} = 1.2U_{\text{eqCArom}}$; $1.2U_{\text{eqN}}$; $1.5U_{\text{eqCmeth}}$).

Theoretical calculations

All calculations were done with Gaussian 09 [11], the B3LYP method and the 6-31+G * basis for all atoms except for cadmium and iodine for which the LanL2DZ pseudopotential was used. In order to understand why the two aromatic rings of aromatic molecules are not in the same plane (the dihedral angle between them is 8.91 °) two calculations were made:

- Optimization of hydrogen atoms only, the other atoms being in the positions defined by the X-rays in order to account for the properties in the solid state;
- Full optimization of the isolated complex in order to account for the properties in solution or in the isolated state.

Each time the infrared spectrum has been calculated (in the case of full optimization it makes it possible to verify that the obtained structure corresponds to a minimum) as well as the HOMO-LUMO and MEP. Mulliken charges are also given.

Table 1 Experimental details of [CdI₂(DMDPy)₂]

Crystal data	
Chemical formula	C ₂₄ H ₂₄ CdI ₂ N ₄
M_r	734.68
Crystal system, space group	Orthorhombic, <i>Pbcn</i>
Temperature (K)	100
a, b, c (Å)	16.248 (3), 10.099 (2), 15.380 (3)
V (Å ³)	2523.7 (8)
Z	4
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	3.33
Crystal size (mm)	0.13 × 0.12 × 0.07
Data collection	
Diffractometer	D8Venture
Absorption correction	Multi-scan
T_{\min}, T_{\max}	0.662, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	21666, 2898, 2282
R_{int}	0.057
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.650
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.025, 0.045, 1.07
No. of reflections	2898
No. of parameters	143
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	0.58, -0.61

Infrared spectroscopy

The IR spectra were recorded in the 4000–400 cm⁻¹ range with a “Perkin–Elmer FTIR” spectrophotometer 1000 using samples dispersed in spectroscopically pure KBr pressed into a pellet.

Hirshfeld surface

The fingerprint plots of contacts around the organic molecule were generated with the CrystalExplorer3.1 software [12]. The analysis of contact types and their enrichment [13] were computed with the MoProViewer program [14]. In order to obtain, in one step, an integral Hirshfeld surface around the two independent ligands, the Cd(II) cation and the two iodine anions, it was computed around an ensemble of moieties which are not in contact with each other in the crystal.

Results and discussion

X-ray diffraction study

The main geometrical features of the different chemical entities of the new cadmium complex $[\text{CdI}_2(\text{DMDPy})_2]$ are reported in Tables 2 and 3. X-ray crystal structure analysis reveals that the complex crystallizes in the orthorhombic space group *Pbcn*. The asymmetric unit of the compound is shown on Fig. 1. It contains a bidentate 4,4'-dimethyl-2,2'-dipyridine organic ligand, one iodine ion and a bivalent metallic cation of cadmium, in a special position, coordinated by four nitrogen atoms N1, N2, N1ⁱ and N2ⁱ (*i*: $-x+1, y, -z+3/2$) from two organic molecules and two atoms of iodine I and Iⁱ to form a slightly distorted CdI_2N_4 octahedron. The dihedral angle between the planes containing the aromatic rings is 8.91° (Fig. 2).

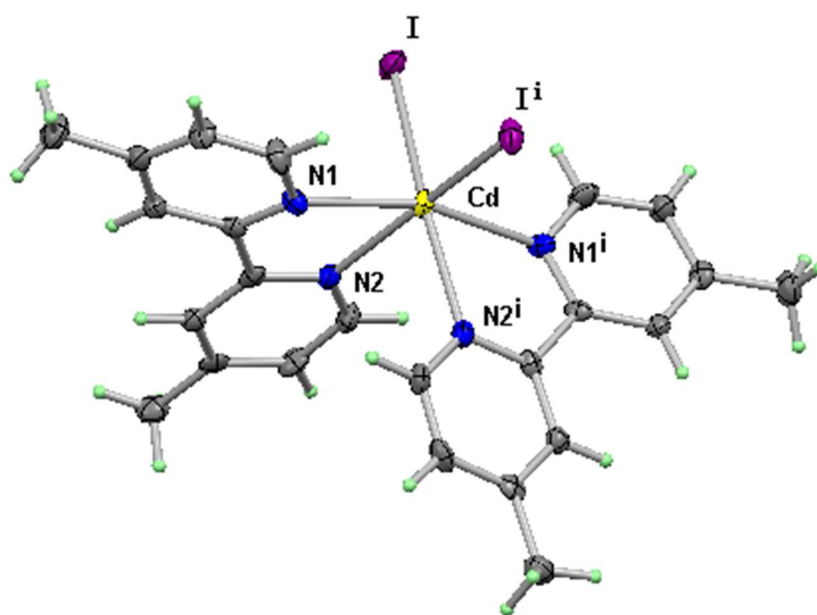


Fig. 1 ORTEP of the title compound with displacement ellipsoids drawn at the 40% probability level. (i: $-x+1, y, -z+3/2$)

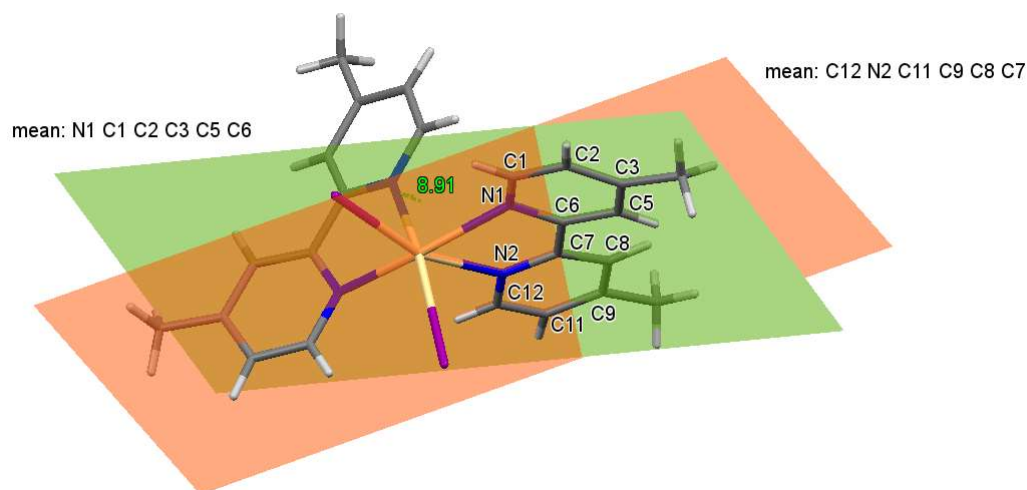


Fig. 2 Dihedral angle between the planes of the two crystallographic independent aromatic rings in the title compound

The geometric characteristics of the bonds in the CdI_2N_4 octahedron are shown in Table 2.

Table 2 Selected bond distances and angles (\AA , $^\circ$) in $[\text{CdI}_2(\text{DMDPy})_2]$

Cd–N1	2.394 (2)	Cd – N1 ⁱ	2.394 (2)
Cd–N2	2.394 (2)	Cd – N2 ⁱ	2.394 (2)
Cd–I1	2.8648 (5)	Cd – I1 ⁱ	2.3949 (4)
N2 – Cd–I1	163.27 (5)	N2 ⁱ —Cd—N1	97.78 (8)
N2 ⁱ - Cd – I1 ⁱ	163.27 (5)	N1—Cd—I1 ⁱ	93.29 (6)
N2 - Cd – I1 ⁱ	89.78 (6)	N1 ⁱ —Cd—I1	93.29 (6)
N2 ⁱ - Cd – I1	89.78 (6)	N1—Cd—I1	97.58 (6)
N2 ⁱ - Cd – N2 ⁱ	82.60 (11)	N1 ⁱ —Cd—I1 ⁱ	97.58 (6)
N2—Cd—N1 ⁱ	97.78 (8)	N1—Cd—N1 ⁱ	162.84 (11)
N2—Cd—N1	68.93 (8)	I1—Cd—I1 ⁱ	101.188 (19)
N2 ⁱ —Cd—N1 ⁱ	68.93 (8)		

The bond lengths around the cadmium cation are Cd–N1 = 2.394 (2), Cd–N2 = 2.393 (2) and Cd–I = 2.8648 (5) \AA . The bond angles around cadmium vary from 68.93 (8) $^\circ$ to 163.27 (5) $^\circ$

and indicate that the coordination geometry of the cadmium atom can be considered as a slightly deformed octahedron. All these distances are within the range of those observed for other hexacoordinated Cd(II) complexes with iodine and nitrogen donor ligands [15, 16]. The projections of the structure of the compound $[\text{CdI}_2(\text{DMDPy})_2]$ along the \vec{a} and \vec{b} directions are given on Figs. 3 and 4 respectively.

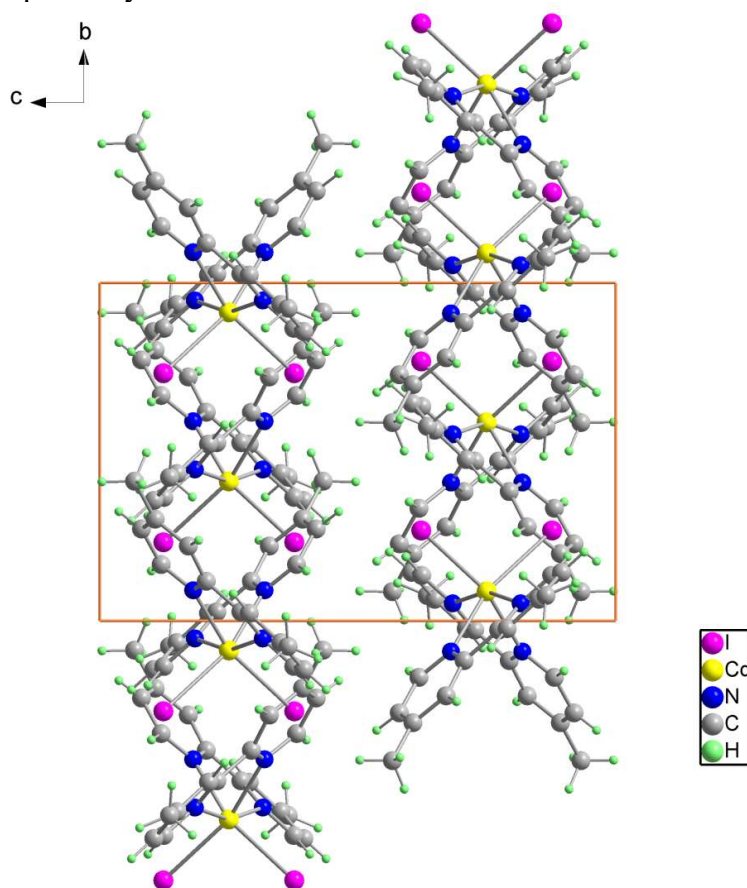


Fig. 3 Projection along the a -axis of the structure of $[\text{CdI}_2(\text{DMDPy})_2]$. Dotted lines indicate hydrogen bonds

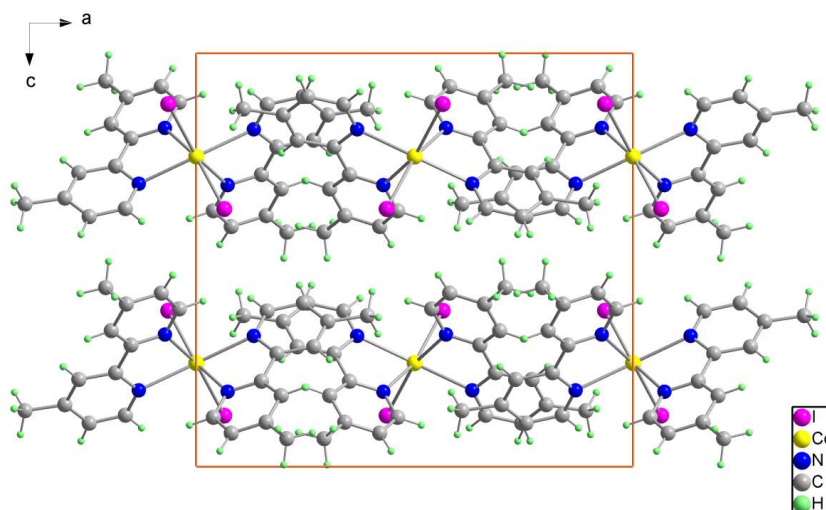


Fig. 4 Projection along the *b*-axis of the structure of $[\text{CdI}_2(\text{DMDPy})_2]$. Dotted lines indicate hydrogen bonds

They show that the complexes are arranged parallel to the (**a**, **b**) plane at $z = \frac{1}{4}$ and $z = \frac{3}{4}$. The robustness of the crystal is enhanced by three intermolecular interactions of the C-H... π type (Fig. 5) between the hydrogen atoms of the methyl groups and of the heterocycle, on one hand, and of the neighboring heterocycle, on the other hand, with H...plane distances of 3.302, 3.650 and 3.742 Å. This result is compatible with those reported in the literature [17-19].

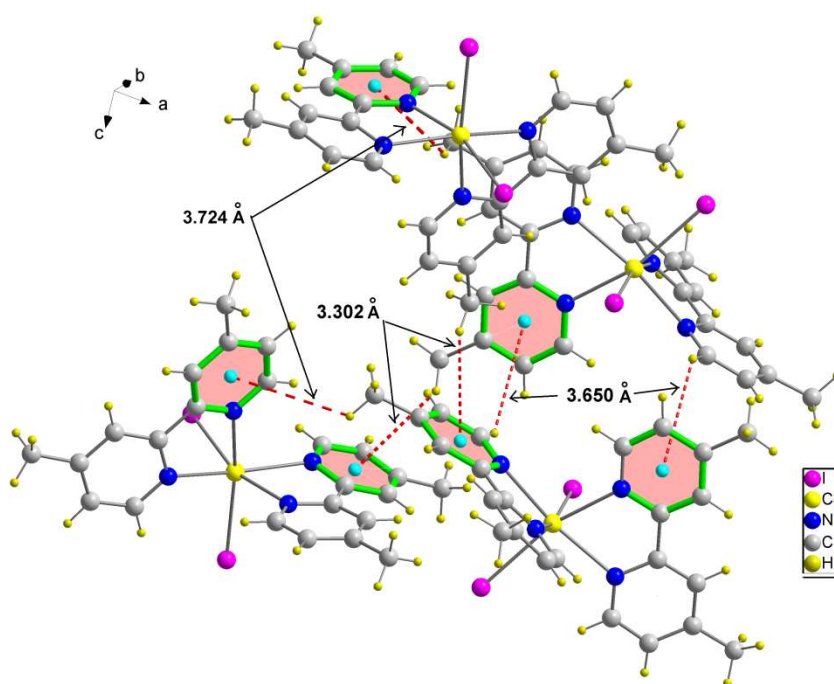


Fig. 5 Intermolecular interactions between neighboring aromatic rings in $[\text{CdI}_2(\text{DMDPy})_2]$.

It is worth to note that the central atom in two similar Cd (II) complexes with the same organic ligand (DMDPy) and with the same halide anion I⁻ $[\text{CdI}_2(\text{DMDPy})(\text{C}_2\text{H}_6\text{OS})]$ [20] and $[\text{CdI}_2(\text{DMDPy})(\text{C}_3\text{H}_7\text{NO})]$ [21] is five-coordinated in a distorted trigonal-bipyramidal configuration, while the Cd(II) atom in the current complex is hexa-coordinated in a distorted octahedral geometry. The pyridine rings in the previous two similar complexes contribute to structural stability through π - π interactions, while the pyridine rings in the title compound $[\text{CdI}_2(\text{DMDPy})_2]$ contribute to structural stability through C-H... π interactions.

Quantum mechanical study

Quantum chemical calculations were performed from the crystal data by using the Gaussian 09 program [11]. Full optimization of the complex results in a great decrease of the angle between the two aromatic rings (to ca. 2° instead of ca. 9°) showing that this twist is due to the structural arrangement in the solid, the solution structure being less distorted.

The HOMO and LUMO of the complex are shown in Fig. 6 for proton positions optimization only and for full optimization. In both cases, the highest occupied orbital (HOMO) is localized on the iodide anions bounded to the cadmium cation, while the lowest unoccupied orbital (LUMO) is localized on one of the organic ligands. The energy gaps of 2.34 and 2.80 eV, respectively, are relatively low, indicating that this material has a semiconductor behavior.

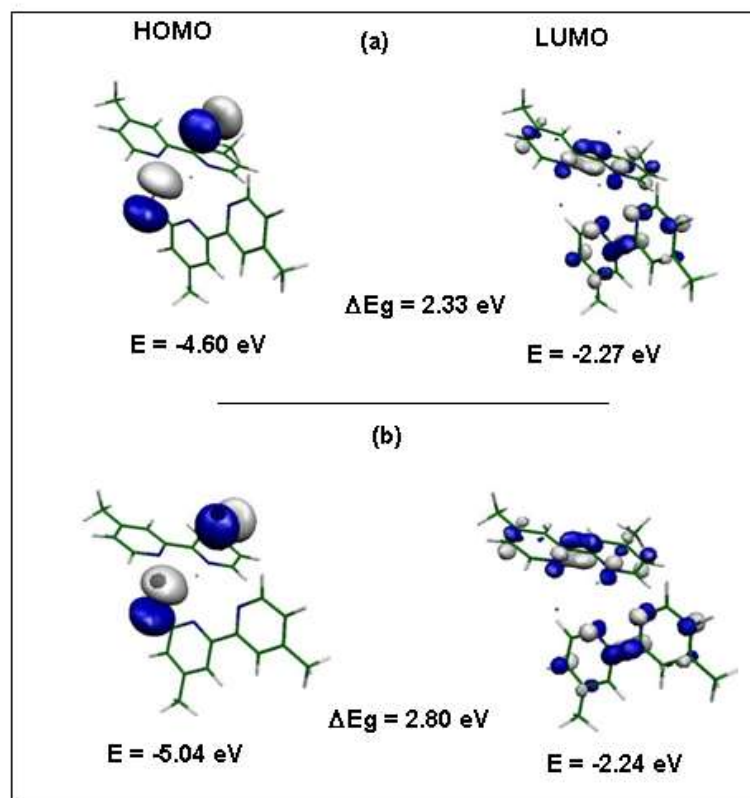


Fig. 6 Frontier orbitals of the isolated complex for proton positions optimization and full optimization.

Molecular Electrostatic Potential analysis

The Molecular Electrostatic Potential (MEP) surface of this compound is depicted in Fig. 7. The MEP is used to determine the nuclear and electronic charge distribution of a given molecule. The maps were obtained at the B3LYP/6-31+G*-LANL2DZ level of theory. Moreover, blue and red colors indicate the positive and negative potentials, respectively. As it can be seen, the electrostatic potential maps are color-coded and are subdivided into many regions. There is no noticeable difference between the two calculations. The most negative zone is located at one of the aromatic carbons, while the positive zones are on the two nitrogen atoms of the aromatic rings.

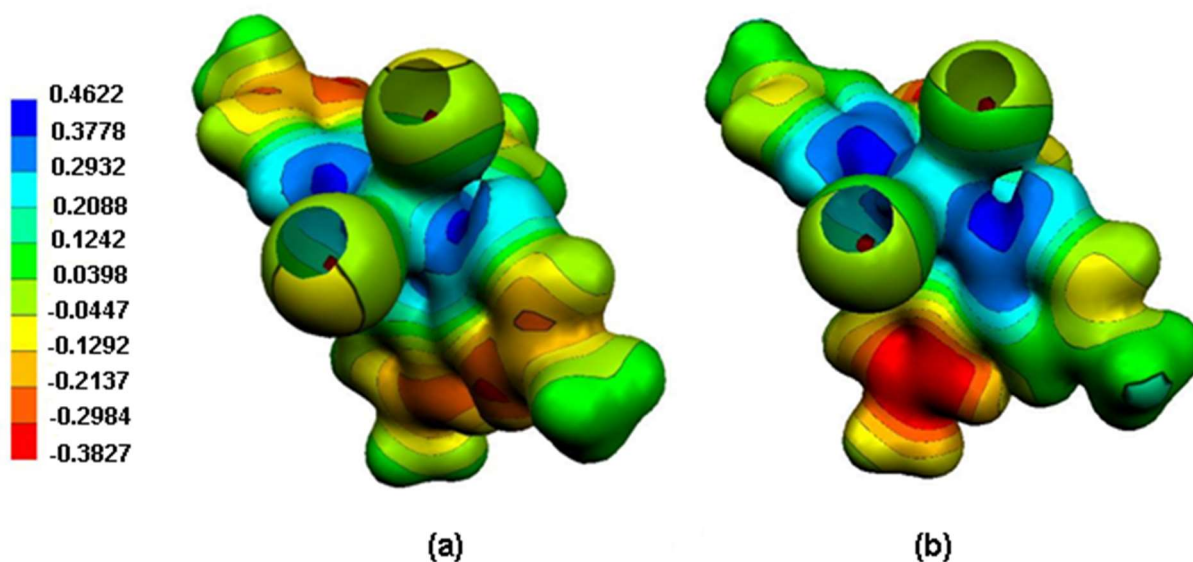


Fig. 7 Molecular Electrostatic Potential maps of $[\text{CdI}_2(\text{DMDPy})_2]$. (a) Optimization of hydrogen atoms only, (b) full optimization of the isolated complex

Mulliken population analysis

The Mulliken charge distribution in the title compound of all atoms, obtained with the same method as above, is given in Table 3. All atoms in the asymmetric unit are listed. The atoms of the organic molecule are numbered as follows:

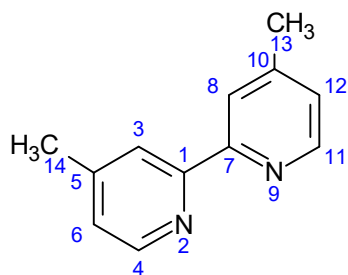


Table 3 Mulliken charge distribution of all atoms in $[\text{CdI}_2(\text{DMDPy})_2]$

Atom	Optimization of protons	Full optimization
Cd	0.178	0.535
I	-0.435	-0.432
N	0.371	0.292
	0.264	0.191
C1-C7	0.168	0.159
	0.401	0.32
C3-C8	-0.761	-0.726
	-0.899	-0.848
H(C3,C8)	0.177	0.176
	0.182	0.176
C5-C10	0.294	0.227
	0.024	0.074
C6-C12	-0.904	-0.95
	-0.857	-0.917
H(C6,C12)	0.197	0.197
	0.192	0.189
C4-C11	0.517	0.627
	0.425	0.511
H(C4,C11)	0.236	0.23
	0.204	0.203
C13-C14	-0.594	-0.64
	-0.641	-0.676
H(C13,C14)	0.241	0.241
	0.211	0.21
	0.223	0.224
	0.244	0.24
	0.223	0.226
	0.208	0.208
Total	0	0

The atomic charge distribution shows that the cadmium ion has a positive charge of 0.178 and 0.535 for the protons and full optimizations, respectively, while the iodide atoms have negative charges of -0.435 and -0.432. For the organic entity, as depicted by the Molecular Electrostatic Potential surface analysis, the nitrogen atoms have a positive charge of +0.371 & 0.264 and +0.292 & +0.191 e. The carbon atoms C3, C8, C13 and C14 have a negative charge in the range -0.594 to -0.899 e. The other carbon atoms have positive charges between +0.024 and +0.627 e. All hydrogen atoms carry positive charge in the range +0.176 to +0.244 e.

3.5. Infrared spectroscopy

Fig. 8-a shows the IR spectrum of $[\text{CdI}_2(\text{DMDPy})_2]$. The most representative and characteristic vibratory modes of this compound can be compared with those of analogous compounds [22, 23]. In the high frequency region, the wide and intense band between 3600 and 2700 cm^{-1} corresponds to valence vibrations $\nu(\text{C-H})$. The bands observed between 1700 and 1100 cm^{-1} are assigned to the valence vibrations $\nu(\text{C}=\text{C})$ of the aromatic ring and $\nu(\text{C-C})$ and $\nu(\text{C-N})$ of the organic ligand. The vibration bands ranging between 1000 and 500 cm^{-1} are attributed to the out-of-plane $\gamma(\text{C-H})$, $\gamma(\text{C-C})$ and $\gamma(\text{C-N})$ deformation modes [24].

The calculated IR spectrum is given in Fig. 8-b. DFT calculations of the frequencies were made on the geometry obtained after optimization of the protons. This spectrum is very similar to the experimental one. A close agreement between the experimental and theoretical wavenumbers ($R^2 = 0.998$) is mostly achieved in the fingerprint region as shown in Fig. 9. Thus, the precision is sufficient to assign the experimental frequencies and to confirm the attributions proposed above.

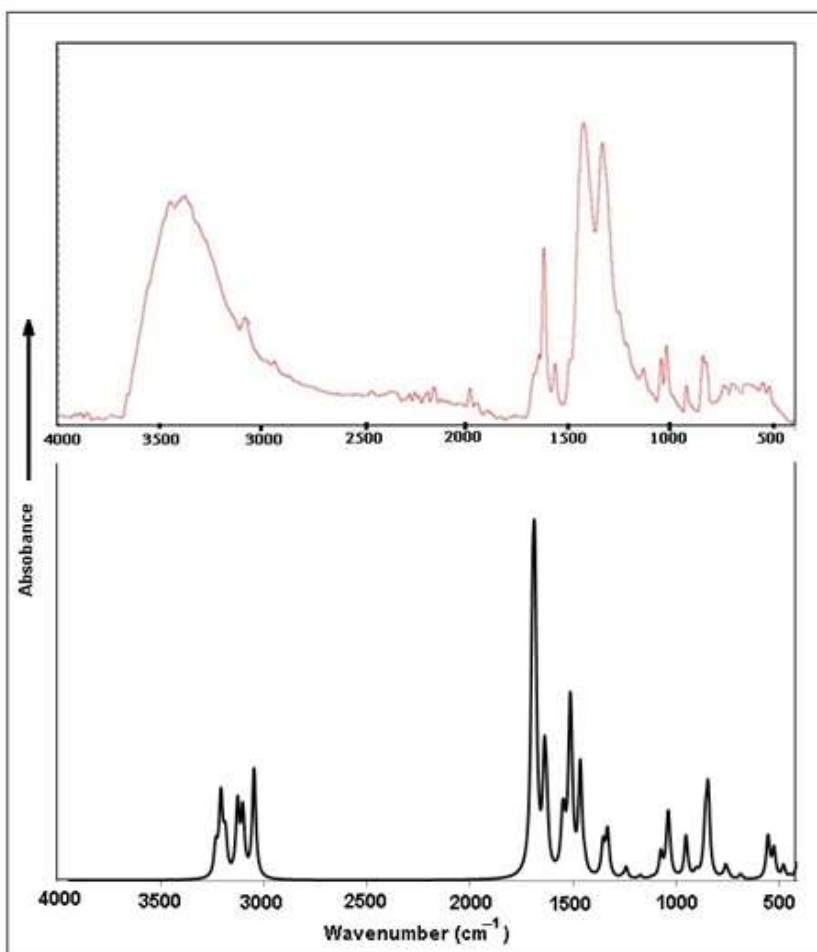


Fig. 8 (a) Experimental Infrared absorption spectrum. (b) Calculated infrared absorption spectrum of $[\text{CdI}_2(\text{DMDPy})_2]$

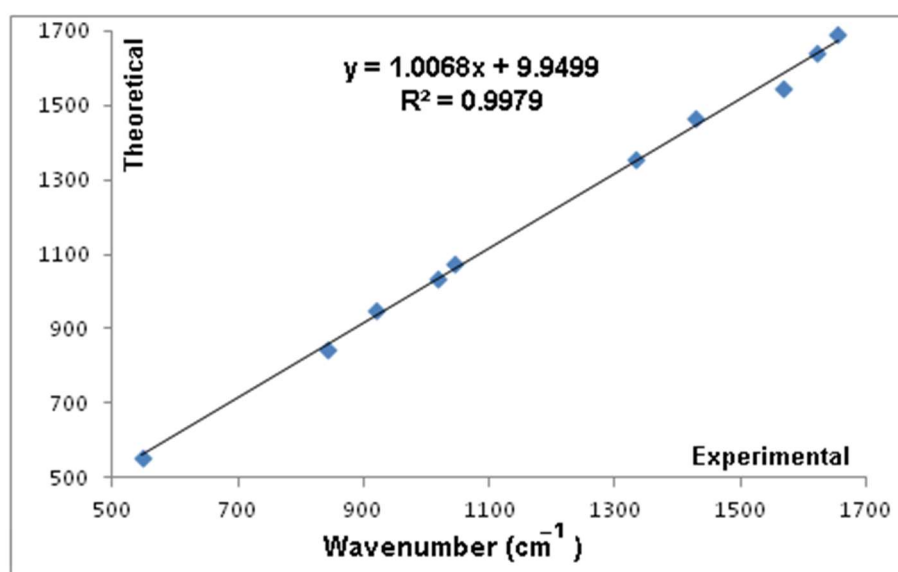


Fig. 9 Comparison between experimental and calculated IR frequencies of $[\text{CdI}_2(\text{DMDPy})_2]$

Hirshfeld surface and contacts enrichment ratio

The Hirshfeld surface is a region in space surrounding the molecules where the chemical nature of their intermolecular contacts can be analyzed. The contact enrichment, derived from the Hirshfeld surface, is computed from the ratio of the actual contacts C_{xy} in the crystal with those computed as if all types of contacts had the same probability to form [25, 26]. The contact enrichment ratio is a powerful tool to deduce which type of contacts are over or under-represented in the crystal packing. An enrichment ratio larger than unity for a given pair of chemical species X...Y indicates that these contacts are favored (over-represented) in the crystal. The analysis of contact types and their enrichment were computed with the MoProViewer program [14].

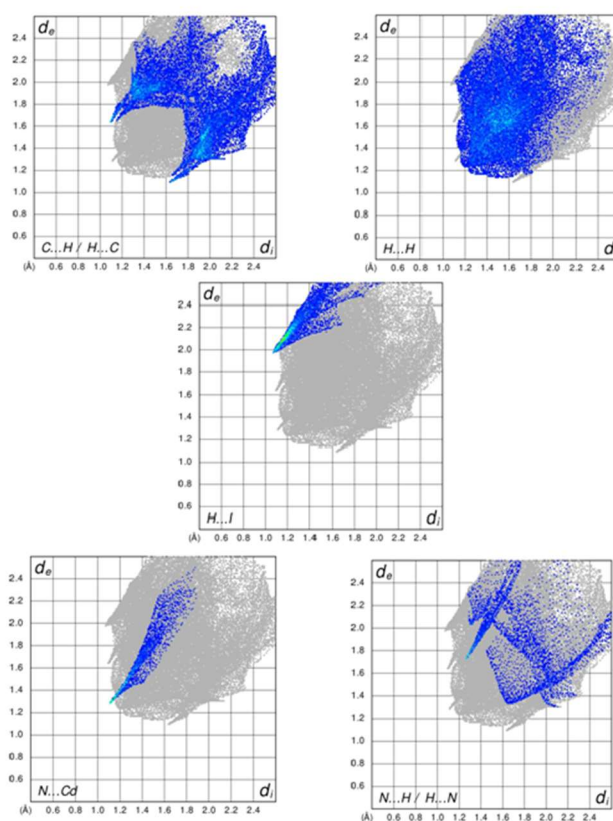


Fig. 10 Hirshfeld surface fingerprint plots of the contacts around the 4,4'-dimethyl-2,2'-dipyridine ligand

The fingerprint plots of internal and external distances (d_i , d_e) obtained from CrystalExplorer3.1 [12] are shown in Fig. 10 for the main contacts. There are no long spikes at short distances as there are no strong H-bond donors (H-N or H-O) in the organic molecule and,

as a consequence, no strong hydrogen bonds. As the two nitrogen atoms have their electron lone pairs directed towards the Cd(II) cation, there are no possibilities of C-H...N hydrogen bonds. The C-H...N contacts occur at longer distance $d(\text{H}\dots\text{N}) > 3.05\text{\AA}$ in the fingerprint plot. The shortest contacts are constituted by C-H...H-C interactions. Small spikes appear for the H...C and H...I weak H-bonds and for the N...Cd coordination.

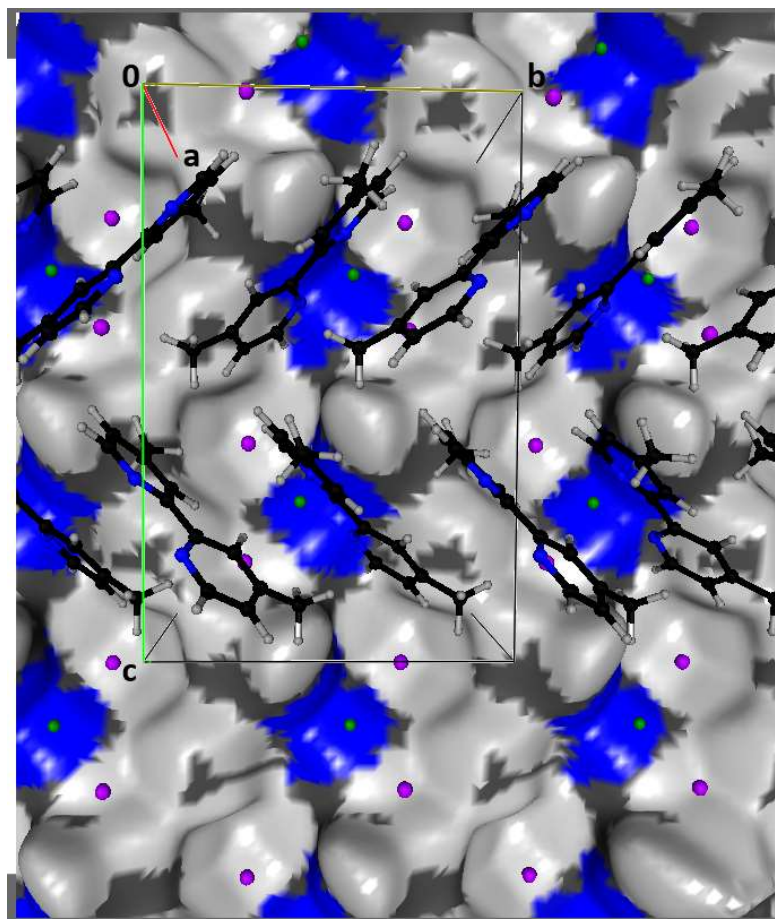


Fig. 11 View of the Hirshfeld surface at the interface between the organic shell and the CdI₂ layer at $x = n + \frac{1}{2}$. The view is a crystallographic autostereogram [14]. The first shell of organic molecules in front of the surface is shown in the central zone. At the top and at the bottom of the view, only the CdI₂ ions are shown. The surface is coloured according to the atom type which is behind. blue: nitrogen, light grey: hydrogen, dark grey: carbon. Cadmium: green spheres, iodide: purple spheres.

The chemical nature of contacts and their enrichment ratios in the title compound are shown in Table 4 and Fig. 11. The Hirshfeld surface of the ensemble is constituted by as much as 41.8% of hydrogen atoms followed by carbon at 26.1%, I (18.5%), Cd(7.8%) and N(5.8%).

The major contacts are constituted by H...I, C...H, H...H and C...C contacts followed by Cd...N and Cd...I coordination. The Cd(II) cation is coordinated by four nitrogen atoms resulting in a high enrichment ratio $E_{CdN} = 8.2$. The metallic cation is also coordinated by two iodine atoms ($E_{CdI} = 2.1$). The C...C contacts display E ratio around 1.5, which highlights the stacking interactions between the aromatic rings. The C...H contacts, corresponding to C-H... π , represent 26.4% of the total area and are also slightly over represented at $E_{CH} = 1.3$.

Table 4 Nature of contacts at the ensemble of Hirshfeld surfaces around organic molecule, iodide and cadmium ions: chemical content on the surface, proportion of contact types and contacts enrichment ratios. Reciprocal contacts X-Y and Y-X were merged. The major contacts C_{XY} are in bold characters. The enrichment values E_{XY} larger than unity are in bold and highlight overrepresented interactions. The lower part of the table shows the major contacts on the Hirshfeld surface around the ensemble of an organic dimer and a CdI₂ moiety.

atom surface %	H	C	N	Cd	I
	41.8	26.1	5.8	7.8	18.5
H	11.4		%	contacts	
C	26.4	9.2			
N	1.5	0.4	0.1		
Cd	0.7	1.5	7.7	0	
I	29.1	3.0	0.9	7.7	0.4
H	0.71			enrichment	
C	1.3	1.5			
N	0.35	0.1	0.34		
Cd	0.09	0.33	8.2	0	
I	1.7	0.29	0.39	2.1	0.10
(dimer_formed)	H...I	H...C	H...H	C...C	
% contact%	35.2	32.5	18	11.8	
enrichment	1.8	1.07	0.67	1.39	

It is worth noting that, as can be seen in Fig. 3, the CdI₂ moieties are in cavities located in layers at $x = n + \frac{1}{2}$ and $x = n$; and so they do not interact with the surrounding CdI₂ groups, as the closest distance is $d(\text{Cd},\text{I})=6.84$ Å. The analysis performed on the Hirshfeld surface around the ensemble of the coordination dimer and CdI₂ moiety gives another perspective of the contacts in the crystal packing (Table 4). From this point of view, the C-H...I weak hydrogen bonds are

the most abundant and most enriched contact type. The other main contacts are H...C, H...H and C...C which are all over represented, except H...H.

Conclusion

A new Cd(II) complex with the 4,4'-dimethyl-2,2'-dipyridine ligand has been prepared at room temperature. In the title compound, the organic entity behaves as a bidentate ligand and Cd(II) adopts a slightly distorted octahedron coordination. The Cd(II) metal coordination complex with four N ligands and two iodine anions results in the formation of the organic molecular dimer in the crystal. The contact enrichment ratios derived from the Hirshfeld surface analysis show that besides the coordination, the crystal packing is also stabilized by aromatic stacking between neighbor aromatic rings and by C-H... π interactions well confirmed by over-represented C...C and C...H hydrophobic contacts. The band gap energy between HOMO and LUMO indicates that the title compound has a semiconductor behavior. The Molecular Electrostatic Potential analysis reveals that the most negative zone is located at one of the aromatic carbons, while the positive zones are on the two nitrogen atoms of the aromatic rings. DFT calculations allow the attribution of the experimental IR bands.

Acknowledgment

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Supplementary data

Crystallographic data for the structural analysis have been deposited at the Cambridge Crystallographic Data Centre, CCDC No 2044251. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK: fax: (+44) 01223-336-033; e-mail: deposit@ccdc.cam.ac.

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