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Synthesis, crystal structure and Hirshfeld surface analysis of the complex compound bis(*o*-phenylenediamine-N,N')-bis(2,4-dihydroxybenzoato-O)-cadmium(II)

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In this paper, the synthesis, crystal structure, Hirshfeld surface analysis, and intermolecular interaction energies of a new complex compound $[Cd(OPD)_2(2,4\text{-}DBA)_2]$ involving Cd(II), *o*-phenylenediamine (OPD), and 2,4-dihydroxybenzoic acid (2,4-DBA) were studied. The resulting complex compound has a symmetrical structure and forms an octahedral shape in space. Its syngony is monoclinic and the space group is $P2_1/n$. In the crystal structure of the molecule, the unit cell parameters are: a = 5.4981(1) Å, b = 19.3609(5) Å, and c = 11.5687(2) Å. Two molecules of OPD are bound to the central atom in a chelate state by donor-acceptor bonds. Two molecules of 2,4-DBA are bound to the central atom in a monodentate state by ionic bonds. The length of the donor-acceptor bonds bound to the central atom in the molecule is 2.36Å. The crystal structure of the molecule contains intra- and intermolecular hydrogen bonds of the N−H•••O and O−H•••O types. The processes of interaction of particles in the molecule were studied based on Hirshfeld surface analysis. Based on the 2D fingerprint di and de functions, it was determined that the interaction of H…H, H…O/O…H and H…C/C…H pairs of atoms occupies the main share in the structure of the molecule. The O−H•••π interactions and intermolecular interaction energies of the molecule were also determined. The total interaction energy of the molecule is -320.1 kJ. The vibrational frequencies of the bonds and functional groups in the resulting complex compound were determined based on Raman spectroscopic analysis.

Keywords: *o*-Phenylenediamine, Crystal structure, Hirshfeld surface analysis, Raman spectroscopic analysis

Bioactive ligands containing oxygen and nitrogen donor atoms are widely used to synthesise complex compounds. *o*-Phenylenediamine (OPD) is one of the most important ligands in coordination chemistry[1]. The adjacent donor nitrogen atoms in *o*-phenylenediamine increase the possibility of forming stable chelates. Also, *o*-phenylenediamine participates in active redox processes due to the unshared electrons of the amino group[2]. Various complex compounds of *o*-phenylenediamine with some d-metals and the (M-L) coordination patterns between them have been studied[3,4]. *o*-Phenylenediamine and complex compounds obtained on its basis are of great importance in medicine and agriculture[5]. It has been found that 2,4-dihydroxybenzoic acid and *o*-phenylenediamine enter into active redox reactions through mobile hydrogen atoms[6]. The structure of metallocomplexes of *o*-phenylenediamine is geometrically diverse and complex[7-9]. In particular, the $[Zn(OPDA)_2(NO_3)_2]$ complex is highly stable due to strong hydrogen bonds and the chelate binding of the OPD molecule to the central atom. The coordination number of the central atom in the complex is 6 and it is located in an octahedral position in space. The crystal structure is monoclinic and the space group is $P2_1/n$. The molecule contains strong intra- and intermolecular hydrogen bonds of the N−H•••O type[10]. The phenomenon of tautomerism occurs in some complex compounds obtained based on *o*-phenylenediamine. For example, the complex compound $[Ni(OPDA)_2(NCS)_2]$ occurs in yellow and purple forms. Yellow single crystals quickly turn into purple crystals when heated in the temperature range of 110-120°C. Both single crystals have the space group P21/c and the presence of N–H•••S hydrogen bonds in the crystal structure[11]. In the complex compound $[Ni^{II}\{C_6H_4(NH_2)_2\}_2(NO_2)_2]$, the conversion to the nitro group was observed under various conditions[12]. The complex compound $[Ni(OPDA)_2Cl_2]$ has a high paramagnetic property. In the crystal structure of the complex, two chlorine atoms and two OPDA molecules are bound to the

central atom in a bidentate state. The molecule has a = 11.2470(3) Å, b = 5.9034(2) Å, c = 12.0886(3) Å, β = 115.143(1)° and a crystal volume of V=726.58(4) Å3. The basic octahedral shape of the molecule is formed by hydrogen bonds of the N−H•••Cl type. These hydrogen bonds connect the molecule to a two-dimensional axis of symmetry[13]. Chelated complexes' higher stability than monodentate complexes has been experimentally proven[14-17]. The complex $[Cd(C_6H_8N_2)_4](C_{10}H_6O_6S_2)$ obtained from the Cd(II) ion in the presence of OPD and naphthalene 1,5-disulfonate is also highly stable. The complex has a monoclinic structure and a C2/c space group. The central atom is surrounded by 4 OPD molecules. 2 OPD molecules are bound to the central atom in a bidentate, chelated state, and 2 OPDs are bound to the monodentate state. The supramolecular structure of the molecule contains hydrogen bonds of the N3—H3A•••O2, N2—H2A•••O2, N1—H1B•••O1, N3—H3B•••O2, N4—H4A•••O1 type[18]. Strong hydrogen bonds also stabilise the crystal structure of the molecule[19]. In the complexes $[Ni(C_6H_8N_2)_2\ (H_2O)_2](C_{10}H_6O_6S_2)$ and $[Zn(C_6H_{14}N_2)_2\ (H_2O)_2]Cl_2$, water molecules in the inner sphere form strong hydrogen bonds with the outer sphere[20,21]. In addition, the electronic energetic properties of the complexes based on *o*-phenylenediamine have been well studied theoretically using DFT methods[22,23].

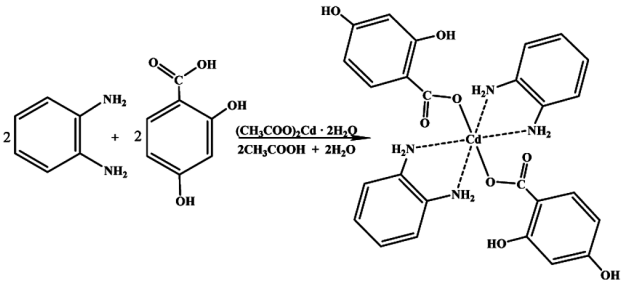
The main aim of this research work is to synthesize a new complex compound $[(Cd(OPD)_2(2,4\text{-}DBA)_2]$ based on Cd(II), *o*-phenylenediamine, and 2,4-hydroxybenzoic acid and to study the composition, crystal structure, and properties of the resulting complex compound.

Experimental Section

For this experiment, cadmium acetate dihydrate crystalline hydrate ($Cd(CH_3COO)_2•2H_2O$), *o*-phenylenediamine and 2,4-hydroxybenzoic acid, and 96% pure ethanol as solvent were used. All of these substances were used in "chemically pure" conditions.

General procedures

The molecular and crystal structure of the complex obtained in this research work was studied using the RTT method in the Olex 2 software package. Also, Hirshfeld surface analysis and intermolecular interaction energies of the complex were studied in the *CrystalExplorer* and *Mercury* programs.



Scheme 1 — Synthesis reaction of the complex compound $[Cd(OPD)_2(2,4\text{-}DBA)_2]$

Synthesis of the complex compound $[(Cd(OPD)_2(2,4\text{-}DBA)_2]$

In the synthesis of this complex compound, the starting materials were: cadmium acetate dihydrate crystalline hydrate ($Cd(CH_3COO)_2•2H_2O$), *o*-phenylenediamine and 2,4-dihydroxobenzoic acid in 1:2:2 molar ratios. 0.1 M solutions were prepared from aqueous solutions of the alcohol and metal salts of the two starting ligands. The solutions were mixed with each other and stirred initially at RT, and then at 55-60℃ for 2 hours on a magnetic stirrer (*p*H 6.5). At the end of the process, the reaction mixture was cooled to RT and left in a constant temperature thermostat (28±1°C) for 12 days. Light yellow, clear crystals were formed with a yield of 80% and samples were selected for RTT. The resulting complex compound The elemental analysis of $C_{26}H_{26}O_8N_4Cd$ is as follows: determined (%) C 49.19, H 4.08, O 20.17, N 8.79, Cd 17.72; found (%) C 49.21, H 4.10, O 20.19, N 8.83, Cd 17.67. The molecular scheme of the resulting $[(Cd(OPD)_2(2.4\text{-}DBA)_2]$ complex is presented in Scheme 1.

Raman spectroscopic analysis

In the Raman spectrum of the powder complex $[Cd(OPD)_2(2,4\text{-}DBA)_2]$, we can see the vibration of the benzene ring in the ring plane at 1773 cm^{-1} and 1777 cm^{-1}. In the region of 1581 cm^{-1}, we can see the deformation vibration of the C=O bond, and in the region of 1188 cm-1, we can see the NH_2- bond. In the regions of 322 cm^{-1} and 359 cm^{-1}, we can observe the M-O and M-N donor-acceptor bonds, respectively.

Also, the Raman spectrum of this complex compound $[Cd(OPD)_2(2,4\text{-}DBA)_2]$ in ethanol (96% solution) was obtained and compared with the Raman spectrum of the powder. The Raman spectrum of the $[Cd(OPD)_2(2,4\text{-}DBA)_2]$ complex in ethanol was also carried out at different time intervals. The obtained

Table 1 — Raman spectrum analysis of OPD in powder form and ethanol solution and the complex compound $[(Ni(OPD)_2(2,4\text{-}DBA)_2]$

Substance	δ (OH)	ν (NH_2)	δ (NH_2)	δ (C=O)	ν (C-N)	Ar (C_6H_6)	M-O	M-N
$[Cd(OPD)_2(2,4\text{-}DBA)_2]$ (powder)	1529	–	1281	1581	1188	1773	359	322
$[(Ni(OPD)_2(2,4\text{-}DBA)_2]$ (ethanol)	1588	–	1287	1619	1193	1826	356	322

Table 2 — Main crystal parameters of the complex compound $[Cd(OPD)_2(2,4\text{-}DBA)_2]$

Parameters	Values	Parameters	Values
Chemical formula	$[Cd(OPD)_2(2,4\text{-}DBA)_2]$	Crystal size, mm	0.00×0.00×0.00
Molecular mass	634.9	Temperature T, °K	293
Syngonium	monoclinic	Scanning range 0, °	4.4, 62.1
Spatial group	P21/n	Interval h,k,l	–6: 5 ; 0: 22 ; –4: 13
a (Å)	5.4981(1)	Total reflexes	3650
b (Å)	19.3609(5)		
c (Å)	11.5687(2)		
α°	90	Number of independent reflexes	1890
β°	92.158(2)		
γ°	90		
V, $Å^3$	1230.59(4)	R_{int}	0.030
Z	5	$F^2 \geq 2\sigma(F^2)$	1521
$D_x g/sm^3$	1.714	Defined parameters	1890
$\mu(CuK_\alpha)$, mm^{-1}	7.634	Structure detection quality	180
R1, wR2(1>2σ(I))	0.0412, 0.1167, 1.03	CCDC - number	2402204
$\Delta_{pmin/max} eÅ^{-3}$	–0.58, 1.34	–	–

results showed that the absorption frequencies of this complex coincided with the Raman spectrum of the powder. This suggests that this complex is stable in ethanol solution (Table 1).

Structural details

The crystal and molecular structure of the complex compound $[Cd(OPD)_2(2,4\text{-}DBA)_2]$ was studied thoroughly using the RTT method (Table 2). The molecular structure of the complex is depicted in Fig. 1. This complex has a symmetrical structure, with a metal atom (Cd(II)) located at the center of inertia. Its coordination number is 6, its hybridization is sp^3d^2 and forms an octahedral shape in space. Its syngony is monoclinic and the space group is $P2_1/n$.. In the crystal structure of the complex, two OPD molecules are bound to the central atom in a bidentate state. A slight twisting and sliding of the OPD molecule relative to the central atom was observed. The Cd1−N1 and Cd1−N2 donor-acceptor bonds are almost the same length (2.360Å). Also, the N1−Cd1−N2 bonds form an acute angle of 69.60°. Two 2,4-DBA molecules are bound to the central atom in a monodentate state, using ionic bonds. There are 4 N---Cd (~2.36Å) and 2 O−Cd bonds between the central atom and

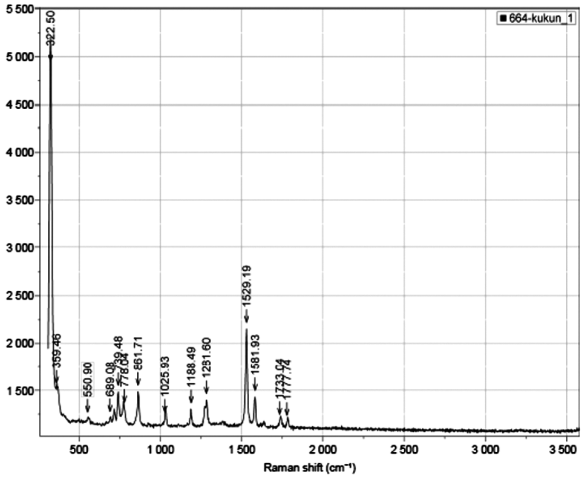


Fig. 1 — Powder Raman spectrum of the complex compound $[Cd(OPD)_2(2,4\text{-}DBA)_2]$.

neighboring atoms. There are bonds of the type (2.342Å). The oxidation state of the central atom in the molecule is +2 (Table 3).

The complex $[Cd(OPD)_2(2,4\text{-}DBA)_2]$ contains intramolecular and intermolecular hydrogen bonds of the N−H•••O and O−H•••O types. Internal hydrogen bonds are formed between the hydrogen atoms of the first hydroxyl group in the 2.4-DBA molecule and the second oxygen atoms of the carboxyl group (O3−H3•••O2). There are also

Table 3 — Bond lengths and bond angles of atoms in the complex compound [Cd(OPD)2(2,4-DBA)2]

№	Length of bond	(Å)	Bond corner	(°)
1	Cd1−O1	2.342(3)	O1−Cd1−N1	88.45(13)
2	Cd1−N1	2.360(4)	O1−Cd1−N2	91.31(13)
3	Cd1−N2	2.365(4)	O1−Cd1−O1_a	180.00
4	Cd1−O1_a	2.342(3)	O1−Cd1−N1_a	91.55(13)
5	Cd1−N1_a	2.360(4)	O1−Cd1−N2_a	88.69(13)
6	Cd1−N2_a	2.365(4)	N1−Cd1−N2	69.60(13)

Table 4 — Hydrogen bond geometry of the complex compound $[Cd(OPD)_2(2,4\text{-}DBA)_2]$

D−H···A	D−H,Å	H−A,Å	D−A,Å	DHA, burchak
N1−H1A···O1	0.901(5)	2.308(5)	2.995(5)	132.9(4)
N2−H2A···O1	0.900(5)	2.173(5)	3.058(5)	167.4(4)
N2−H2B···O2	0.901(5)	2.364(5)	3.036(5)	131.4(4)
O3−H3···O2	0.821(4)	1.89(4)	2.588(5)	143(3)
O4−H4···O1	0.822(2)	1.90(2)	2.712(4)	168(4)

Symmetry codes: -x,1-y,1-z# 1+x,y,z# 1-x,1-y,1-z# -1/2+x,3/2-y,1/2+z# 3/2-x,1/2+y,1/2-z# 1/2+x,3/2-y,-1/2+z# -x,1-y,-z# -1/2+x,3/2-y,-1/2+z# 1/2+x,3/2-y,1/2+z# -1+x,y,z# 3/2-x,-1/2+y,1/2-z# -3/2+x,3/2-y,-1/2+z# 3/2+x,3/2-y,1/2+z

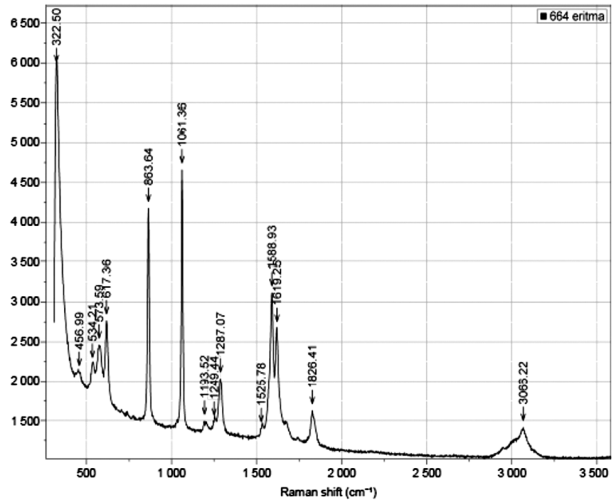


Fig. 2 — Raman spectrum of the synthesized [Cd(OPD)2(2,4-DBA)2] complex compound in ethanol

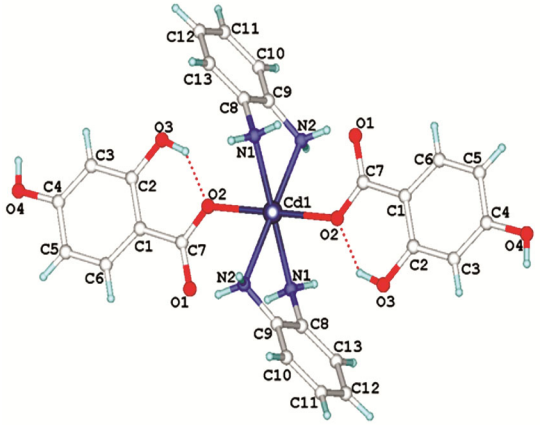


Fig. 3 — Molecular structure of the complex compound [Cd(OPD)2(2,4-DBA)2] (hydrogen bonds are shown by dotted lines).

zigzag intramolecular hydrogen bonds between the amino groups in the OPD molecule and the first oxygen atoms in 2.4-DBA (N1−H1A•••O1 and N2−H2A•••O1). The D−H, Å and D−A, Å parameters are almost the same in both hydrogen bonds, but the H−A, Å and DHA (angle) values are slightly different (Table 4). Intermolecular hydrogen bonds form between the first oxygen atom of the carboxyl group in 2,4-DBA and the second hydroxyl group in the second molecule (O4−H4•••O1) (Fig. 2, Fig. 3 and Fig. 4).

Supramolecular features and Hirshfeld surface analysis

Currently, CrystalExplorer, Mercury, and ab initio non-empirical computational methods are widely used

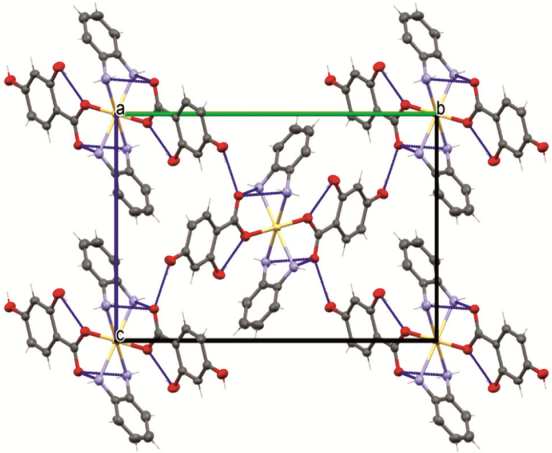


Fig. 4 — Crystal structure of the complex compound $[Cd(OPD)_2(2,4\text{-}DBA)_2]$. (The dotted lines indicate intramolecular and intermolecular hydrogen bonds.)

to interpret particle interactions in complex compounds[24]. Hirshfeld surface analysis allows us to visualize the arrangement of molecules in the crystal unit cell and the interaction of particles[25]. Red spots on the Hirshfeld surface of the complex $[Cd(OPD)_2(2,4\text{-}DBA)_2]$ in terms of dnorm represent interactions close to the van der Waals radius. Blue spots represent interactions far away from the van der Waals radius. The standard deviations of the surface spots range from -0.6708 to 1.1024. The Hirshfeld surface area of the molecule is 513.06Å² and the Hirshfeld surface volume is 606.19Å³. Due to the presence of strong hydrogen bonds in the molecule, they are mainly displayed as red spots on the Hirshfeld surface (Fig. 5a). In the complex compound $[Cd(OPD)_2(2,4\text{-}DBA)_2]$, red spots are mainly formed by the electron clouds of the hydroxyl group (OH) of the 2,4-DBA molecule. In addition, the processes of interaction of pairs of atoms in the molecule were studied. The main interactions in the molecular structure correspond to the share of H…H, H…O/O…H and H…C/C…H pairs of atoms. This quantitatively determined the contribution of pairs of atoms to the energetic arrangement of molecules. Also, weak intermolecular π–π interactions can be seen in the crystal arrangement of this molecule. Strong π–π interactions in the crystal unit cell are mainly manifested in molecules with aromatic rings located along parallel axes[26,27]. The complex $[Cd(OPD)_2(2,4\text{-}DBA)_2]$ contains strong O–H•••π interactions with a distance of 3.374 Å (Fig. 5b, Fig. 6). These interactions are important in the structure of the molecule and in ensuring its stability.

The intermolecular distances and bond interaction energies in the crystal lattice of the complex compound $[Cd(OPD)_2(2,4\text{-}DBA)_2]$ were calculated using the Mercury 3.8 program (Fig. 7 and Fig. 8). Accordingly, the intermolecular energies of the complex compounds located at distances of 5.073, 11.5369, 11.4533, 11.5537, 13.9816 and 13.781 Å are -148.342, -34.4578, -23.7009, -17.9757, -8.54829 and -6.54829 kj/mol, respectively. The total bond energy of the molecules in the crystal unit cell is -330.1 kj/mol. It was found that the larger the intermolecular distances in the crystal unit cell of the complex compounds, the lower their total interaction energy[28-33].

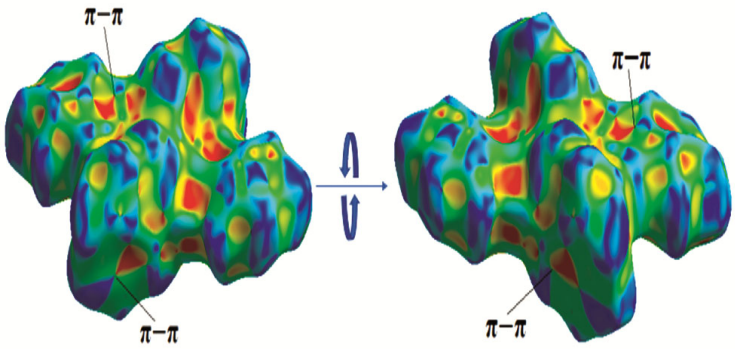


Fig. 5 — Hirshfeld surface area of the complex compound $[Cd(OPD)_2(2,4\text{-}DBA)_2]$ according to the shape index

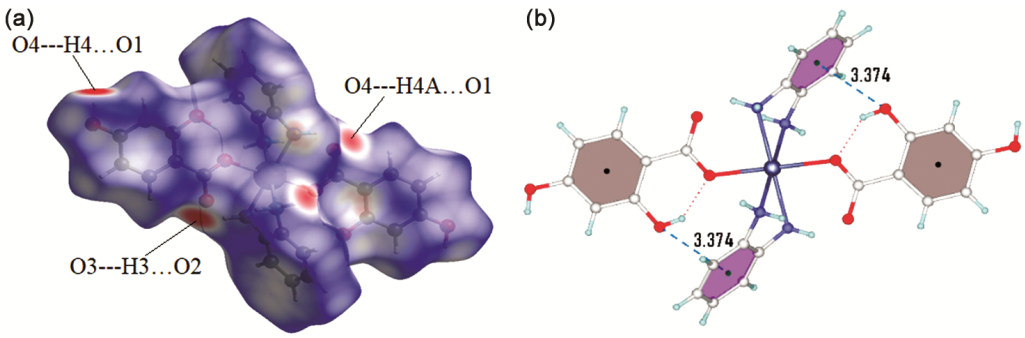


Fig. 6 — Hirshfeld surface area (a) and O–H•••π interactions in the molecule according to the d_{norm} of the complex compound $[Cd(OPD)_2(2,4\text{-}DBA)_2]$

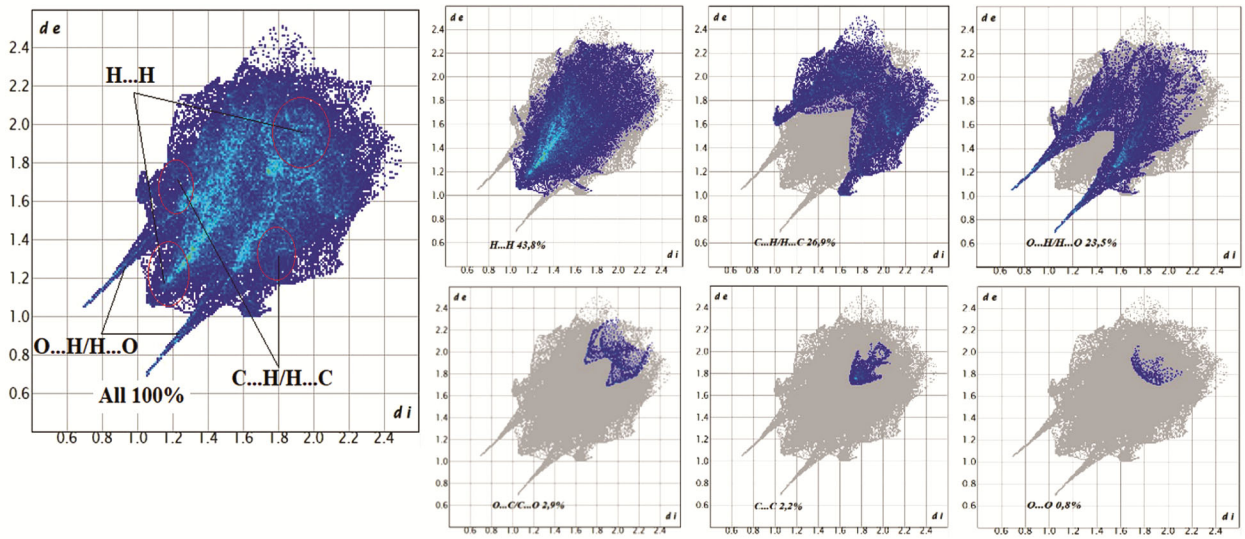


Fig. 7 — 2D fingerprint image of the complex compound $[Cd(OPD)_2(2,4\text{-}DBA)_2]$

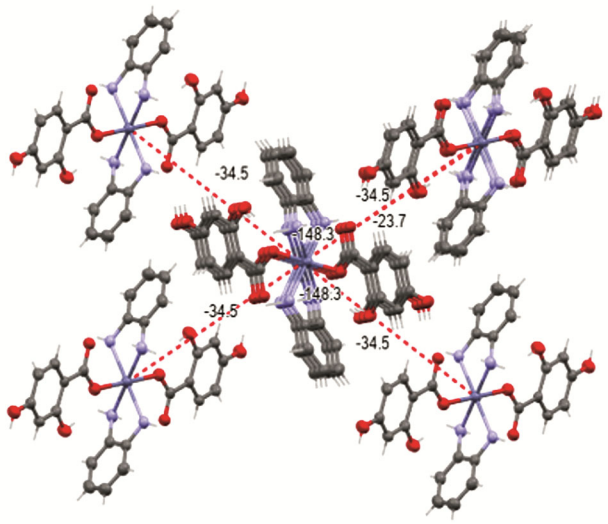


Fig. 8 — Intermolecular interaction energies in the crystal unit cell of the complex compound $[Cd(OPD)_2(2,4\text{-}DBA)_2]$

Conclusion

In conclusion, a new complex compound $[Cd(OPD)_2(2,4\text{-}DBA)_2]$ was synthesized based on *o*-phenylenediamine. The molecular and crystal structure of the obtained complex compound was studied using the RTT method. The molecule has a symmetrical structure, with a metal atom located at the centre of symmetry. The length of the Cd1N4 donor-acceptor bonds around the central atom is 2.360-2.365 Å. The Cd1O2 ionic bonds are 2.342 Å. Also, the interaction processes of the particles in the obtained complex compound were studied based on Hirshfeld surface area analysis. The Hirshfeld surface area volume is V=606.19Å^3 and the surface area is S=513.06Å^2. The vibrational frequencies of the functional groups and bonds in the obtained complex compound in ethanol solution were compared and analyzed with the vibrational frequencies in the powder state.

Supplementary Information

Supplementary information is available in the website http://nopr.niscpr.res.in/handle/123456789/58776.

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References

1 Alaqeel S I, *J Saudi Chem Soc*, 21 (2017) 229.
2 Huang M R, Li X G, Yang Y, *Poly Degrad Stab*, 71 (2000) 31.
3 Bittner M M, Lindeman S V, Popescu C V & Fiedler A T, *Inorg Chem*, 53 (2014) 4047.
4 Ahmed A A, BenGuzzi S A, El-Hadi A A, *J Sci Appl*, 1 (2007) 79.
5 Muthirulan P, Rajendran N, *Surf Coat Technol*, 206 (2012) 2072.
6 Tao Y, Han L, Han Y & Liu Z, *Spectrochim Acta A Mol Biomol Spect*, 137 (2015) 1078.
7 Yusuf S S, Salga M S, Sani M, *Sci World J*, 13 (2018) 65.
8 Djebli Y, Boufas S, Bencharif L, Roisnel T & Bencharif M, *Acta Cryst E*, 68 (2012) m1411.
9 Yang B, Zhang G, Niu Q, Liu S, Li H, Chen S & Xu K, *J Solid State Chem*, 317 (2023) 123656.
10 Durdibaeva R, Beknazarov K, Nomozov A, Demir M, Berdimurodov E, *Kuwait J Sci,* 52 (2024) 100341.

11 Supriya S, Das S K, *J Chem Sci*, 122 (2010) 731.
12 Sabbani S, Das S K, *Inorg Chem Comm*, 12 (2009) 364.
13 Willett R D, Gomez-Garcia C J, Twamley B, Gomez-Coca S & Ruiz E, *Inorg Chem*, 51 (2012) 5487.
14 Keene T D, Hursthouse M B, Price D *J, Acta Crystallogr E*, 59 (2003) m1131.
15 Gafurjanovna Y M, Khudoynazarovich T K, Ugli N A K & Ergashevna T I, *Indian J Chem*, 63 (2024) 579.
16 Muratov B A, Turaev K K, Umbarov I A & Nomozov A K, *Int J Eng Trends Tech*, 72 (2024) 202.
17 Nomozov A K, Beknazarov K, Khodjamkulov S, Misirov Z & Yuldashova S, *Baghdad Sci J*, 22 (2024) 458.
18 Shaymardanova M, Mirzakulov K, Melikulova G, Khodjamkulov S, Nomozov A & Toshmamatov O, *Baghdad Sci J*, 21 (2024) 3996.
19 Chen Z L, Zhang Y Z, Liang F P, *Acta Cryst E,* 62 (2006) m1296.
20 Ariyananda W G P, Norman R E, *Acta Cryst E*, 61 (2005) m187.
21 Spielvogel K D, Coughlin EJ, Petras H, Luna JA, Benson A, Donahue C M, Kibasa A, Lee K, Salacinski R, Bart S C, Shaw S K, Shepherd J J & Daly S R, *Inorg Chem*, 58 (2019) 12756.
22 Suyunov J, Torambetov B, Turaev K, Kadirova S, Alimnazarov & Ashurov J, *Acta Cryst E*, 79 (2023) 1190.
23 Wang C F, Li D-P, Chen X, Li X-M, Li Y-Z, Zuo J-L & You X-Z, *Chem Comm*, 2009 (2009) 6940. (https://doi.org/10.1039/B916637H).
24 Suyunov J R, Turaev K K, Alimnazarov B K, Nazarov Y E, Mengnorov I J, Ibragimov B T & Ashurov J M, *Acta Cryst* E, 79 (2023) 1083.
25 Yue S M, Xu H-B, Ma J-F, Su Z-M, Kan Y-H & Zhang H-J, *Polyhedron*, 25 (2006) 635.
26 Afroz Z, Alam M J, Zulkarnain, Faizan M, Ahmad A & Ahmad S, *AIP Conf Proc*, 1731 (2016) 1.
27 Ahatov A A, Turaev K K, Tillaev K R, Kasimov S A & Nomozov A K, *Indian J Chem***,** 64 (2025) 353.
28 Hobza P, *Annu Rep Sect C Phys Chem*, 107 (2011) 148.
29 Seth S K, *Acta Cryst E*, 74 (2018) 600.
30 Nazarov Y E, Turaev K K, Suyunov J R, Alimnazarov B K, Rasulov A A, Ibragimov B T & Ashurov J M, *Struc Rep*, 80 (2024) 1049.
31 Ahatov A A et al, *Indian J Chem*, 63 (2024) 1036.
32 Suyunov J R, Turaev K K, Alimnazarov B K, Ibragimov A B, Mengnorov I J, Rasulov A A & Ashurov J M, *IUCrData*, 8 (2023) x231032.
33 Nomozov A K, Eshkaraev S C, Jumaeva Z E, Todjiev J N, Eshkoraev S S & Umirqulova F A, *Int J Eng Trends Tech*, 72 (2024) 312.