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Synthesis, structure and molecular Hirshfeld surface analysis of polymeric cadmium(II) complex involving tetradentate N_3S-donor ligand and dicyanamide as bridging ligand

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One new polymeric cadmium(II) complex $\{[Cd(bdmpe)(\mu_{1,5}\text{-dca})]ClO_4.CH_3OH\}_n$ has been synthesized by the reaction of cadmium perchlorate with ligand *N*,*N*-bis((3,5-dimethyl-*1H*-pyrazol-1-yl)methyl)-2-(phenylthio)ethan-1-amine (bdmpe) in presence of dca (dicyanamide, $N(CN)_2^-$) as bridging ligand in methanol and characterized by spectroscopic techniques. Single crystal X-ray diffraction study of the complex confirmed that it has polymeric 1D chain and each cadmium centre has distorted octahedral geometry with N_5S coordination and is bonded through two terminal nitrile group of the dca ligand using $\mu_{1,5}$ coordination modes. Intermolecular interactions and packing modes of the compound are described by Hirshfeld surface analysis and two dimensional finger print plots.

Keywords: Cadmium(II), N_3S-donor ligand, Bridging ligand, Polymeric complex, Hirshfeld surface analysis

Synthesis, characterization and structure of polymeric complexes with bridging ligand is an important area of research in chemistry. There are many reports on the synthesis and characterization with structure of polymeric divalent transition metal complexes with large bridging ligand such as dicyanamide (dca) $\{N(CN)_2^-\}$ or carboxylate ligand in presence of bidentate or tridentate organic ligands[1-20]. Recently, there are few reports on synthesis and characterization with structure of the N_3- and N_4- coordinate pyrazolyl containing polymeric metal complexes such as Cu(II), Ni(II), Co(II) and Cd(II) with large bridging ligand dicyanamide[21,22]. It has been reported that pyrazolyl containing N_4-coordination ligand shows interesting coordination behaviour and formed polymeric complex in presence of cadmium perchlorate and thiocyanate ion[23]. As we are interested in the synthesis and structural characterization polymeric bivalent metal complexes with pyrazolyl containing ligand, we would like to check the coordination behaviour pyrazolyl containing N_3S-donor ligand as well as bridging mode of dca in presence of cadmium perchlorate.

Here in this paper, we report the synthesis and structural characterization of polymeric cadmium(II) complex$\{[Cd(bdmpe)(\mu_{1,5}\text{-dca})]ClO_4.CH_3OH\}_n$ with pyrazolyl containing N_3S coordinate ligand in presence of bridging dca ligand . Intermolecular interactions and packing modes of the compound is described by molecular Hirshfeld surface analysis.

Materials and Methods

The chemicals and solvents used were analytical grade and purchased from commercial sources. 2-chloroethan-1-amine hydrochloride and thiophenol (Aldrich) were reagent grade and used as received. Cadmium(II) perchlorate hexahydrate was prepared by treatment of cadmium(II) carbonate with dilute perchloric acid, followed by slow evaporation of the solution on steam bath. (3,5-dimethyl-1H-pyrazol-1-yl)methanol[24], 2-(arylsulfanyl)ethyl-1-amine[25] and *N*,*N*-bis((3,5-dimethyl-*1H*-pyrazol-1-yl)methyl)-2-(phenylthio)ethan-1-amine (bdmpe) were synthesized using reported procedures[26].

The FT-IR spectrum was recorded on Bruker alpha FT-IR spectrometer using KBr pellet. The micro analysis (C, H and N) were carried out using a Perkin-Elmer IA 2400 series elemental analyser.

Synthesis of metal complex

Preparation of complex $\{[Cd(bdmpe)(\mu_{1,5}\text{-dca})]ClO_4.CH_3OH\}_n$

A solution of ligand bdmpe (0.093 g, 0.25 mmol) in methanol (10 mL) was added to a solution of cadmium perchlorate hexahydrate# (0.091 g, 0.25 mmol) in methanol (20 mL) with stirring at room temperature. The colour of the solution changed to light yellow upon addition of the ligand to the cadmium(II) solution. A solution of sodium dicyanamide (0.022 g, 0.25 mmol) in methanol (5 mL) was added slowly to the metal-ligand solution after 5 min and the solution was stirred at room temperature for 3 h, filtered and allowed to evaporate the solvent slowly at room temperature. Light yellow coloured crystals were collected by filtration and dried. Yield: 0.130 g (76%); Elemental analysis (%) for $C_{23}H_{31}N_8O_5ClSCd$, Calculated (Found): C, 40.65 (40.35); H, 4.47 (4.52); N, 16.50 (16.29).

Results and Discussion

Synthesis

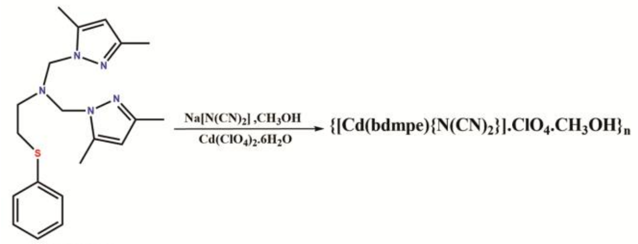
Polymeric octahedral cadmium(II) complex has been synthesized with good yield (75%) (Scheme 1) by the reaction of the ligand *N*,*N*-bis((3,5-dimethyl-*1H*-pyrazol-1-yl)methyl)-2-(phenylthio)ethan-1-amine (bdmpe), cadmium salt and sodium dicyanamide in methanol at room temperature. The molecular composition of the complex was confirmed by microanalysis and FT-IR. The presence of ClO_4^- ion outside the coordination sphere was confirmed by IR and single crystal X-ray diffraction studies. Crystal structure of complex shows that it is a polymeric complex and each cadmium centre has octahedral geometry and two cadmium centres are bridged by $\mu_{1,5}$-dicyanamide ion. The complex is insoluble in water but soluble in organic solvents like acetonitrile, DMSO, DMF etc.

FT-IR spectroscopy

Bonding of ligand N,N-bis((3,5-dimethyl-1H-pyrazol-1-yl)methyl)-2-(phenylthio)ethan-1-amine (bdmpe) in the complex was confirmed by comparing the IR spectrum of ligand and the complex. Both the complex and ligand have common absorption bands at ~1555 cm^{-1} for the ν(C=C) of the phenyl ring, ~1468 cm^{-1} for the ν(C=C) and ν(C=N) of the pyrazole ring and the thioether stretching frequency around 691 cm^{-1} indicating the co-ordination of the ligand to the cadmium centre. The spectrum exhibits three strong bands in the region of 2177 to 2287 cm^{-1}, one strong at 2177 cm^{-1} due to ν_s(C≡N) and two weak bands in the range of 2254 and 2287cm^{-1} due to ν_{as}(C≡N) and $\nu_s+\nu_{as}$(C≡N) bridging dca ligand in the complex[27]. The spectrum of the complex exhibits a broad band at 1089 $cm^{-1}$and a weak δ(O-Cl-O) band at 625 cm^{-1} for the non-coordinating $\nu(ClO_4^-)$[28]. One broad band exhibited in the region of 3440 cm^{-1} is due to ν(OH) of the methanol molecule.

X-ray crystallographic analysis

Details of data collection and important features of the structure refinement parameters for the complex are given in Table 1. Data was collected on Oxford



bdmpe

Scheme 1 — Synthesis of the polymeric Cd(II) complex.

Table 1 — Crystallographic parameters of {[Cd(bdmpe)(μ-$_{1,5}$dca)]$ClO_4.CH_3OH$}$_n$

Empirical formula	$C_{22}H_{25}CdClN_8O_5S$
Formula weight	677.46
Temperature (K)	293
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	10.5033(7)
b (Å)	26.008(2)
c (Å)	11.0841(9)
α (°)	90.00
β (°)	98.037(7)
γ (°)	90.00
Volume (Å^3)	2998.1(4)
Z	4
ρ_{calc} (g/cm^3)	1.465
μ (mm^{-1})	0.931
F (000)	1336.0
Crystal size (mm^3)	0.23 × 0.21 × 0.1
Radiation	MoKα (λ = 0.71073)
2θ range for data collection (°)	7.28 to 57.82
Index ranges	$-13 \le h \le 7$ $-34 \le k \le 34$ $-14 \le l \le 14$
Reflections collected	13017
Independent reflections	6551 [R_{int} = 0.0287, R_{sigma} = 0.0470]
Data/restraints/parameters	6551/0/347
Goodness-of-fit on F^2	1.068
Final R indexes [I>=2σ (I)]	R_1 = 0.0584, wR_2 = 0.1524
Final R indexes [all data]	R_1 = 0.0828, wR_2 = 0.1695
Largest diff. peak/hole (e Å^{-3})	1.14/-0.70
CCDC number	1948112

#***Caution!*** Metal complexes with perchlorate ion are potentially explosive and should be synthesized in small quantities and handled with utmost care.

X-CALIBUR-S diffractometer equipped with graphite-monochromatized Mo-Kα radiation (λ = 0.71073 Å) at 293 K. The data interpretations were processed with CrysAlisPro, Agilent Technologies, Version 1.171.35.19 [29]. An absorption correction based on multi-scan method was applied[30]. The structure was solved by direct method and refined by the full-matrix least-square based on F^2 technique using SHELXL-97 program package[31]. All calculations were carried out using WinGX system Ver-1.64 [32]. All non-hydrogen atoms were refined anisotropically. The positions of the hydrogen atoms were added to their geometrically ideal position. ORTEP3 for Windows program were used for generating for molecular graphics.

Description of crystal structure of{[Cd(bdmpe)($\mu_{1,5}$-dca)]ClO_4.CH_3OH}$_n$

An ORTEP diagram with the atom labelling scheme of Cd(II) complex is shown in Fig. 1 and selected bond parameters are given in Table 2. The structural data shows each cadmium centres in the polymeric compound has N_5S coordination environment with distorted octahedral geometry and two cadmium centres is bridged by nitrile group of bridging μ-1,5-dca. The molecule has monoclinic crystal system with $P2_1/n$ space group.

Monomeric structure of the complex (Fig. 1a) shows each cadmium is surrounded by three nitrogen

Table 2 — Bond length (Å) and bond angles (º) of the Cd(II) complex

Bond	Bond length	Bond	Bond angle
Cd1-S1	2.808(16)	N6-Cd1-N8	95.10(2)
Cd1-N3	2.329(4)	N6-Cd1-N5	109.40(2)
Cd1-N1	2.491(4)	N8-Cd1-N5	92.73(18)
Cd1-N5	2.320(4)	N6-Cd1-N3	105.82(18)
Cd1-N6	2.208(5)	N8-Cd1-N3	91.80(17)
Cd1-N8	2.279(5)	N5-Cd1-N3	143.88(17)
		N6-Cd1-N1	168.01(18)
		N8-Cd1-N1	96.77(19)
		N5-Cd1-N1	71.75(16)
		N6-Cd1-S1	72.13(13)
		N8-Cd1-S1	91.95(15)
		N5-Cd1-S1	169.49(16)
		N3-Cd1-S1	92.27(13)
		N6-Cd1-S1	78.76(11)
		N8-Cd1-S1	76.0610)

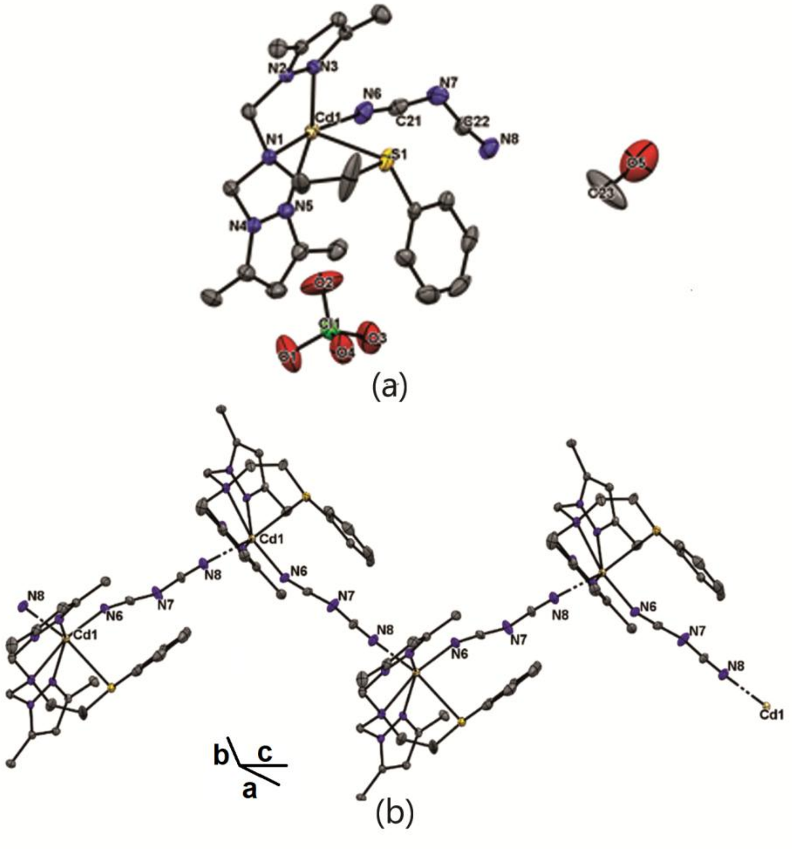


Fig. 1 — (a) ORTEP diagram depicting the structure of mononuclear Cd(II) complex with atom numbering scheme (40% probability factor for the thermal ellipsoids) and (b) Polymeric 1D structure of the complex along c-axis

atoms N5, N1, N3 and one sulphur atom S1 of the ligand bdmpe and two nitrogen atoms N6 and N8 of two bridging dca ligand. Each cadmium centre has octahedral geometry and is surrounded by four nitrogen atoms N1, N5, N3 and N6 in the equatorial positions and S1 and N8 atoms are in the axial position. The bond distances in the equatorial positions Cd-N1 (2.492 Å), Cd-N5 (2.321 Å) Cd-N3 (2.329 Å) and Cd-N6 (2.208 Å) are not equal and the axial bond distance Cd-S (2.809 Å) is much longer than Cd-N8 (2.279 Å). Unequal bond lengths in the coordination sphere produce distortion in the molecule. Each asymmetric unit contains one non coordinated ClO_4^- ion and one methanol molecule.

In the polymeric complex, each cadmium centre is bonded through N atoms of the two nitrile groups of bridging dca ion and ligand bdmpe. Two cadmium centres are joined by bridging dca ligand through Cd-N6-C21-N7-C22-N8-Cd bonding and the bridge is not linear but V-shaped. The bond distances of dca ion are Cd-N6 (2.208 Å), N6-C21 (1.125 Å), C21-N7(1.270 Å), N7-C22 (1.2992 Å), C22-N8 (1.124 Å) and N8-Cd (2.279 Å). Phenyl group is nearly parallel to the bridging dca ion and N_3S donor ligand is acting as blocking ligand. The angle between two bridging dca ions N6-Cd1-N8 is 95.09º. The intra-chain Cd–Cd distance in the complex is 8.482 Å which is longer than Cd----Cd distances in N_4-coordinated ligand (8.307 Å).

Molecular Hirshfeld surface analysis

Hirshfeld surface analysis[33] is an important tool to understand intermolecular interactions and packing modes in the title compound. This analysis was performed using Crystal Explorer 17.5 program[34]. The 3D Hirshfeld surfaces were mapped over the d_{norm} using a high (standard) surface resolution in the range of -0.5444 to 1.4965 a.u. The generated surfaces are presented with surface transparency to enable better visualization. The electrostatic potential surfaces are plotted with red region which is a negative electrostatic potential (hydrogen acceptors) and blue region which is a positive electrostatic potential (hydrogen donor). The normalized contact distance d_{norm} is the ratio encompassing the distances of any surface point to the nearest interior (d_i) and exterior (d_e) atom and the van der Waals' radii of the atom. These surfaces represent the intermolecular contacts by different colours and colour intensity such as strong, neutral and weak interactions involved in the stabilization of crystal structure were visualized as red, white and blue colors, respectively. Another two colour coded properties e.g. shape index and curvedness were also mapped in the range of -1.00 to +1.00 a.u. and -4.00 to +4.00 a.u., respectively. The shape index is extremely sensitive to the change in surface shape. The curvedness is a measure of the shape of the surface area of the molecule. Further 2D fingerprint (FP) plot with combination of d_e and d_i provides summary of intermolecular contacts in the crystal. The breakdown of FP into specific atom---atom contacts in a crystal provides the types of intermolecular contacts experienced by the molecule quantitatively.

The d_{norm} Hirshfeld surface plot of the complex is shown in Fig. 2a. The bright and large deep red spots in the d_{norm} mapping indicate the close contacts with strong hydrogen bonding. The primary hydrogen bonding interactions in the molecular crystal is found to be N-H···O, O-H···C and N-H···S hydrogen bonding. The red triangles on the shape index (Fig. 2b) represented by concave regions indicate π-stacking interactions whereas the blue triangles represented by convex regions indicate the ring atoms of the molecule inside the surface. The red triangles on the shape index mapping refer to the C-H···π interaction and the bow-tie patterns indicate π···π interaction. The curvedness (Fig. 2c) indicates the electron density of surface curves around the molecular interactions. The flat areas of the surface correspond to low value of curvedness, while sharp curvature area correspond to high values of curvedness and usually tend to divide the surface into patches, indicating contacts between neighbouring molecules. The large flat region delineated by a blue outline refers to π-π stacking interactions. The intermolecular interactions in the polymeric complex is depicted in Fig. 2d.

The two dimensional (2D) fingerprint plots from Hirshfeld surface analyses of the title compound is shown in Fig. S1 (Supplementary Data) which illustrate the relative contribution (in %) of the major intermolecular contacts associated with it. The 2D Finger print plots complement the Hirshfeld surface by summarizing the nature and type of intermolecular contacts in a quantitative manner. The most important interaction is H···H with contribution of 44.0% to the overall crystal packing. Further, the N···H (17.3%), C···H (15.4%), O···H (15.4%) and S···H (2.3%) FP plots also reveal the information regarding the intermolecular interaction with individual

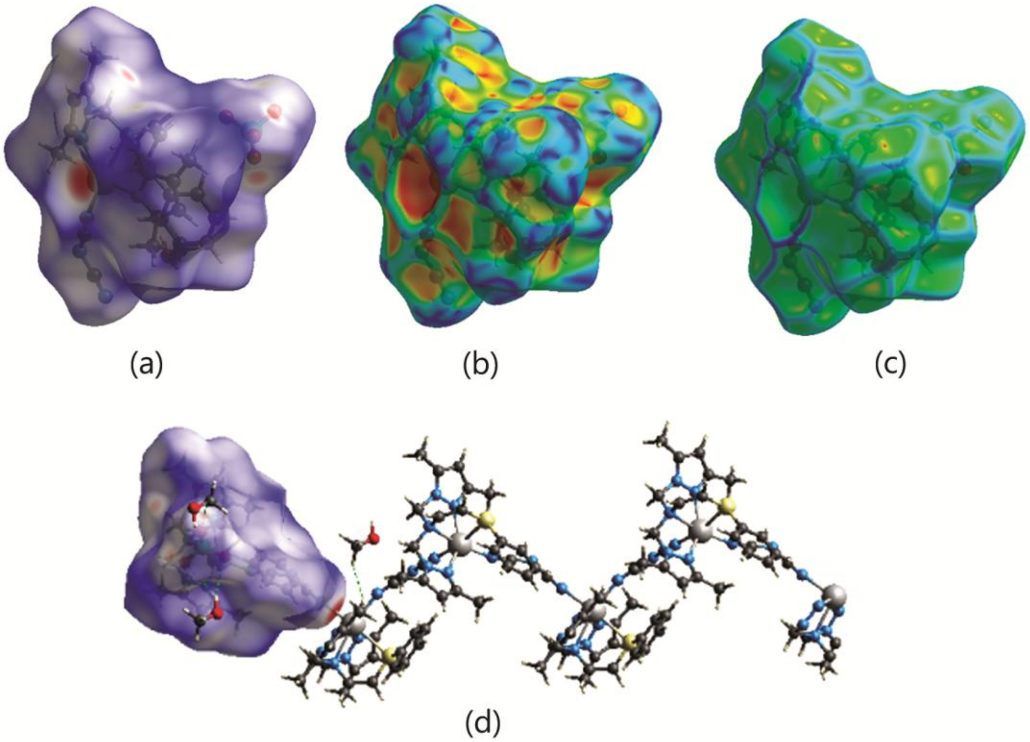


Fig. 2 — Hirshfeld surfaces mapped for (a) d_{norm} surfaces (b) shape index (c) curvature (d) the intermolecular interactions in the polymeric Cd(II) complex

Table 3 — Summary of various contacts and their contributions to the overall Hirshfeld surface

Types of contacts	Contribution (%)
H···H	44.0
N···H	17.3
C···H	15.4
O···H	15.4
S···H	2.3
Cd···N	2.7
N···O	0.3
N···N	1.3
N···C	0.1
C···C	0.2
C···O	1.0
C···S	0.1
C···N	0.1

contribution towards crystal packing. The Cd···N interaction which interlinked the monomer unit contributes 2.7% in the overall crystal packing. The FP plot of C-H contacts shows characteristics “wings” which are identified as a result of weak C-H···π interactions. All the atom···atom contacts with their relative contribution is summarized in Table 3. The Hirshfeld surface analysis reveals hydrogen bonding and H···H interaction as the primary structural motifs that constitute the backbone of the supramolecular arrangement. In addition to that weak C-H···π and π···π interactions govern the solid state packing of the molecular crystal.

Conclusions

One new polymeric cadmium(II) complex $\{[Cd(bdmpe)\{N(CN)_2\}]ClO_4.CH_3OH\}_n$ has been synthesized using N_3S donor tetradentate ligand and characterized with structure. Structural data shows each cadmium centre is bonded by nitrogen atoms of the two nitrile groups with most common μ-1,5 coordination mode and N_3S ligand bdmpe acts as blocking ligand. Each unit cell contains one non bonded ClO_4^- ion and one methanol molecule. Hirshfeld surface analysis of the compound revealed that H···H interaction as the primary intermolecular force of stabilization in addition to the contribution of N···H, C···H and O···H contacts.

Supplementary Data

Supplementary data associated with this article are available in the electronic form at http://nopr.niscair.res.in/jinfo/ijca/IJCA_60A(05)663-668_SupplData.pdf.

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