CHAPTER-5(A)

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

Abstract

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 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 $\mu_{1,5}$-dca ligand. Intermolecular interactions and packing modes of the compound are described by Hirshfeld surface analysis and two-dimensional finger print plots.

5(A).1. Introduction

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{$N(CN)_2^-$} in presence of bidentate and 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)(µ1,5-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.

5(A).2. Experimental

5(A).2.1. Materials

The chemicals and solvents 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 the treatment of cadmium(II) carbonate with dilute perchloric acid and followed by slow evaporation of the solution on steam bath. (3,5-dimethyl-1H-pyrazol-1-yl)methanol [24], 2-(arylsulfany)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 procedure [26].

5(A).2.2. Synthesis of Ligand

5(A).2.2.1. Synthesis of N,N-bis((3,5-dimethyl-1H-pyrazol-1-yl)methyl)-2-(phenylthio)ethan-1-amine (bdmpe)

N, N–bis ((3,5-dimethyl-1H-pyrazol-1-yl)methyl)-2-(phenylthio)ethan-1-amine (bdmpe) was synthesized as per the published procedures [26].

Yield. 1.53 g (92%). Found C = 65.75, H = 7.25, N = 18.78%, Elemental analysis calc. for $C_{20}H_{27}N_5S$: C = 65.01, H = 7.37, N = 18.95%. ^{1}H NMR(400 MHz, $CDCl_3$, 20 ^OC). δ/ppm: 7.2–7.5 (m, 5H, phenyl ring), 5.9 (s, 2H, –CH-/pz ring), 4.9 (s, 4H, $-CH_2-$), 2.89–2.93 (t, 2H, JH_Z = 7.6, 6.8 Hz, $-CH_2-CH_2-N$), 2.72–2.76 (t, 2H, JH_Z = 6.8, 7.6 Hz, $-CH_2-NH_2$), 2.20 (s, 6H,- CH_3/pz ring), 2.18 (s, 6H,CH_3/pz ring).

5(A).2.3. Synthesis of Complex

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

5(A).2.3.1. {[Cd(bdmpe)($\mu_{1,5}$-dca)]ClO_4.CH_3OH}$_n$

A solution of ligand bdmpe (0.093g, 0.25mmol) in methanol (10 ml) was added to a solution of cadmium perchlorate hexahydrate (0.091g, 0.25mmol) 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 (0.022g, 0.25mmol) in methanol (5ml) was added slowly to the metal-ligand solution after 5 min and stirred the solution at room temperature for 3h, filtered and allowed to evaporate the solvent slowly at room temperature. Light yellow coloured crystals were collected by filtration and dried.

Yield. 0.130g (76%). Found C = 40.35, H = 4.52, N = 16.29%. Anal calc for $C_{23}H_{31}N_8O_5ClSCd$: C= 40.65, H = 4.47, N = 16.50%. IR(KBr pellet) cm^{-1}: ν(N-H), 3220; νs(C≡N), 2169s, νas(C≡N), 2234 and νs+νas(C≡N), 2300; ν(C=C), 1601; ν(C=C)+ν(C=N)/pz ring, 1552 s, 1468 s; ν(ClO_4^-), 1078br: δ(O-Cl-O), 644s.

5(A).2.4. Physical Measurements

The FT-IR spectra was recorded on Bruker alpha FT-IR spectrometer using KBr pellet. ^{1}H NMR spectra were recorded on Bruker NMR AV400.The micro analysis (C, H and N) were carried out using a Perkin-Elmer IA 2400 series elemental analyser.

5(A).3. X-ray Crystallography

Details of data collection and important features of the structure refinement parameters for the complex is given in Table 5(A).1 and selected bond lengths (Å) and angels (º) are given in Table 5(A).2. Data was collected on Oxford 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 [27]. An absorption correction based on multi-scan method was applied [28]. 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 [29]. All calculations were carried out using WinGX system Ver-1.64 [30]. 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.

5(A).4. Results and discussion

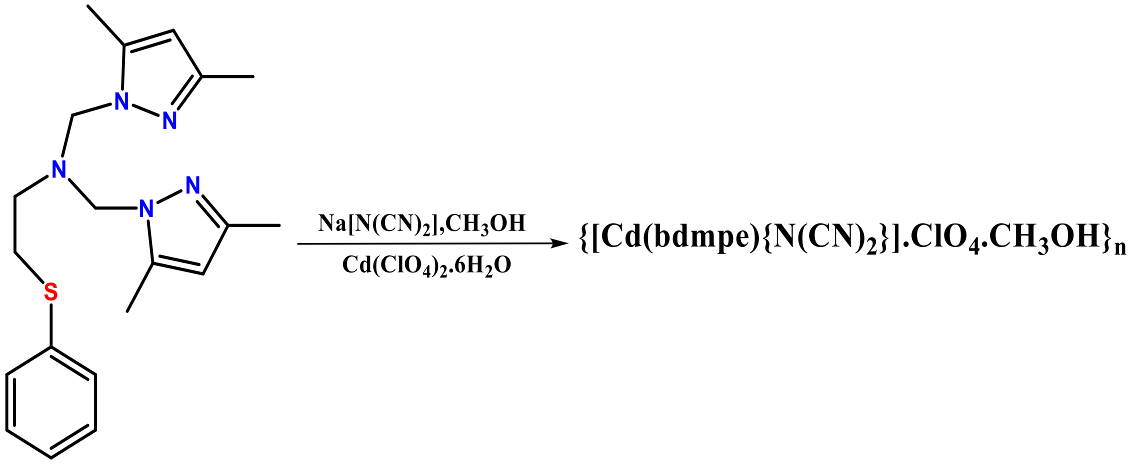
5(A).4.1. Synthesis

Polymeric octahedral cadmium (II) complex has been synthesized by the reaction of the ligand *N*,*N*-bis((3,5-dimethyl-*1H*-pyrazol-1-yl)methyl)-2-(phenylthio)ethan-1-amine (bdmpe), cadmium perchlorate salt and sodium dicyanamide in methanol at room temperature with good yield (77%) [Scheme 5(A).1]. 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 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.

Table 5(A).1 Crystal parameters of Cd(II) complex

	{[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 No.	1948112



bdmpe

Scheme-5(A).1. Synthesis of the polymeric Cd(II) complex

5(A).4.2. Spectral Data

5(A).4.2.1. IR spectral Data

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) + 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 exhibit three strong bands in the region of 2177 to 2287 cm^{-1}, one strong at 2177 cm^{-1} due to νs(C≡N) and two weak bands in the range of 2254 and 2287 cm^{-1} due to the ν(C≡N) of bridging dca ligand in the complex [31]. The IR 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 ν(ClO_4^-) [32]. One broad in the region of 3440 cm^{-1} is due to ν(OH) of the methanol molecule [Fig.5(A).1].

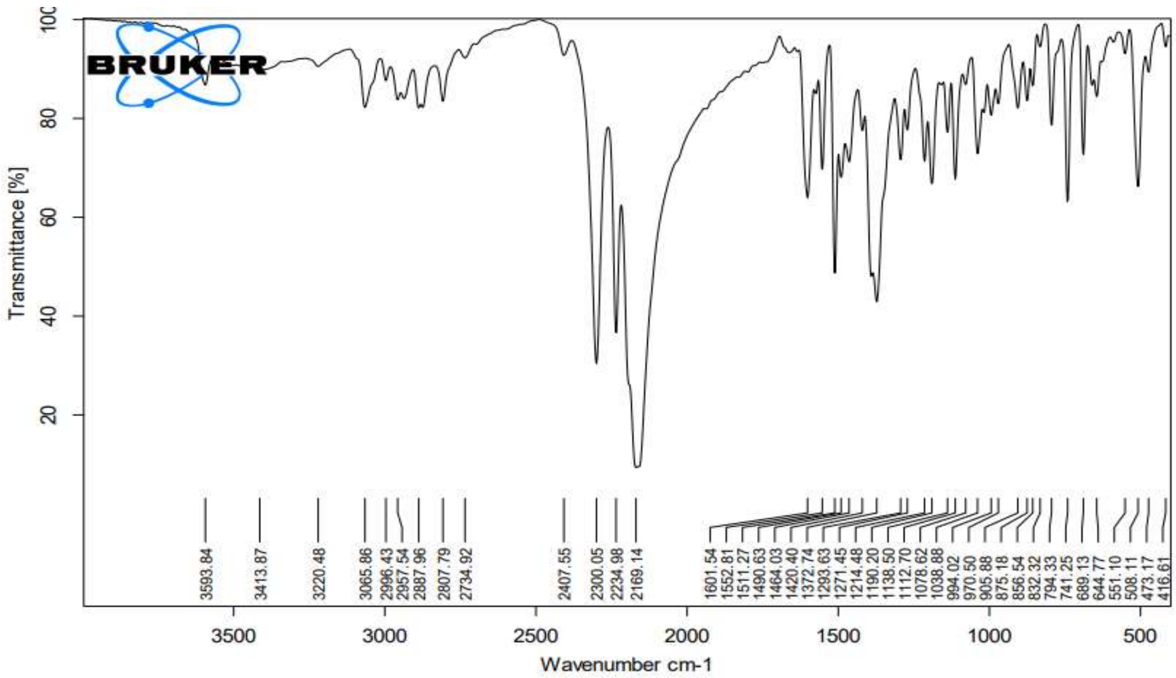


Figure 5(A).1. IR spectrum of $\{[Cd(bdmpe)(\mu_{1,5}\text{-}dca)]ClO_4.CH_3OH\}_n$

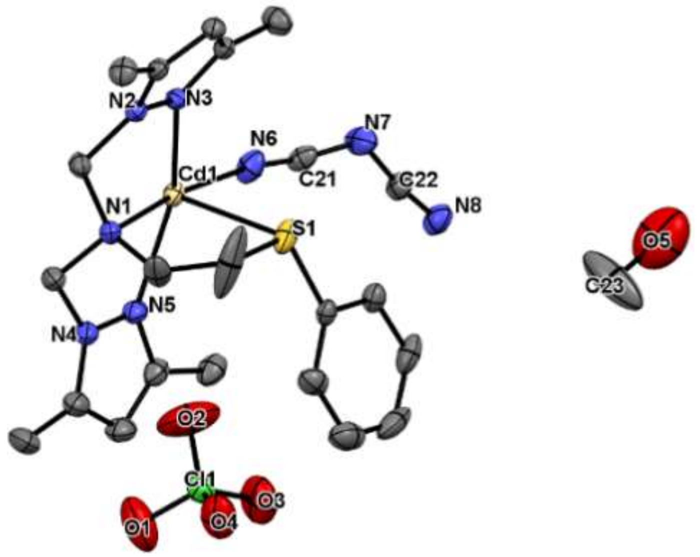
5(A).4.3. Structure of the complex

5(A).4.3.1. Description of structure of $\{[Cd(bdmpe)(\mu_{1,5}\text{-}dca)]ClO_4.CH_3OH\}_n$

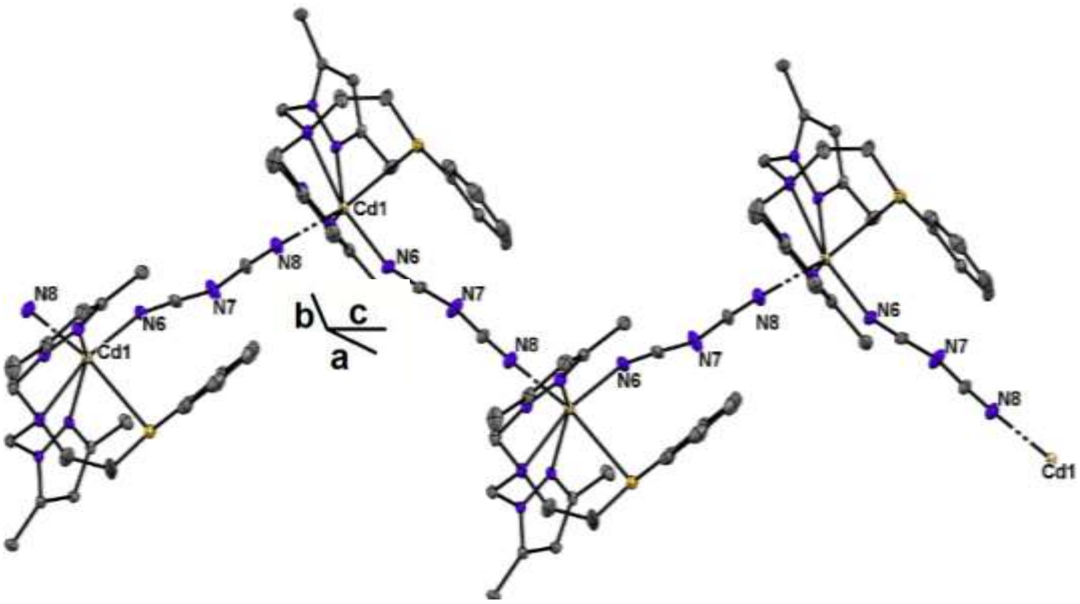
An ORTEP diagram with the atom labelling scheme of Cd(II) complex is shown in Fig. 5(A).2 and selected bond parameters are given in [Table 5(A).2]. The structural data shows each cadmium centres in the polymeric compound has N_5S coordination environment with distorted octahedral geometry and two cadmium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

Asymmetric structure of the complex [Fig. 5(A).2(a).] shows each cadmium is surrounded by three nitrogen atoms N5, N1, N3 and one sulphur atom S1 of the ligand bdmpe and two nitrogen atoms N6 and N8 of two bridging dicyanamide ligand. In the octahedral geometry, each cadmium centre 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 (2.492Å), Cd-N5 (2.321Å) Cd-N3 (2.329Å) and Cd-N6 (2.208Å) are different and the axial bond distance Cd-S (2.809Å) is much longer than Cd-N8 (2.279Å). 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.



(a)



(b)

Figure. 5(A).2(a). ORTEP diagram of the complex with atom numbering scheme (40% probability factor for the thermal ellipsoids). (b). Polymeric 1D structure of the complex along c-axis.

In the polymeric complex, each cadmium centre is bonded through N atoms of the two nitrile groups of bridging dicyanamide ion and ligand bdmpe. Two cadmium centres are joined by bridging dca ligand through Cd-N6-C-N7-C-N8-Cd bonding and the bridge is not linear but v-shaped. The bond distances of dicyanamide ion are Cd-N6 (2.208Å),

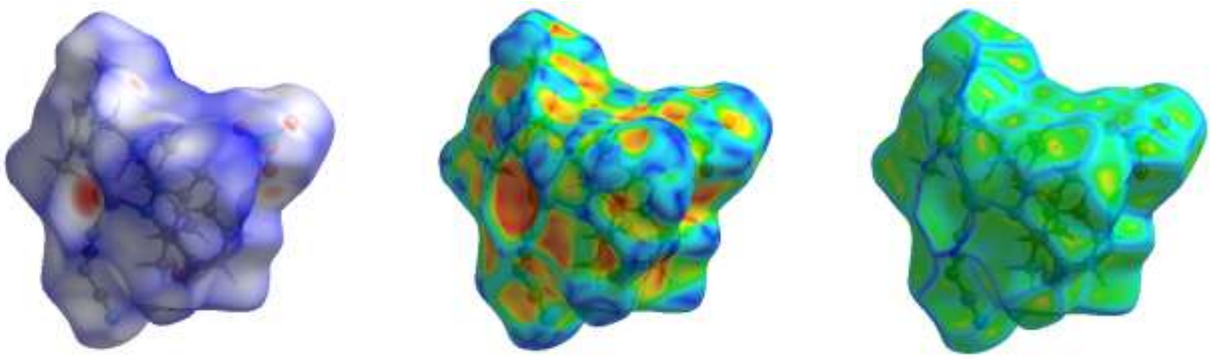
N6-C21 (1.125Å), C21-N7 (1.270Å), N7-C22 (1.2992Å), C22-N8 (1.124Å) and N8-Cd (2.279Å). Phenyl group is nearly parallel to the bridging dicyanamide ion and N_3S donor ligand is acting as blocking ligand. The angle between two bridging dca ions N6-Cd1-N8 is 95.09^0. The intra-chain Cd-----Cd distance in the complex is 8.482 Å which is longer than Cd----Cd distances in N_4-coordinated ligand (8.307Å) [21].

Table 5(A).2 Bond lengths (Å) and angels (º) of Cd(II) Complex

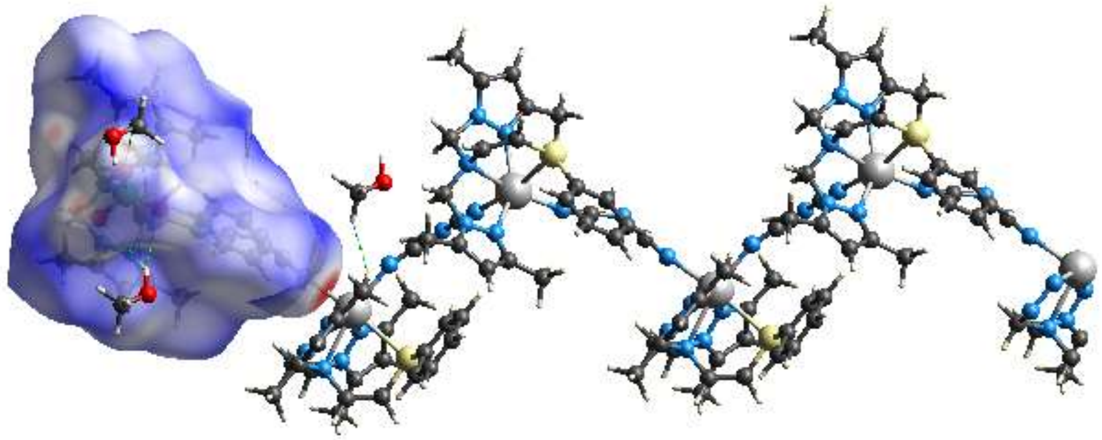
Bond lengths (Å)		**Bond angles (º)**	
Cd1-S1	2.8088(16)	N6-Cd1-N8	95.1(2)
Cd1-N3	2.329(4)	N6-Cd1-N5	109.4(2)
Cd1-N1	2.491(4)	N8-Cd1-N5	92.73(18)
Cd1-N5	2.320(4)	N6-Cd1-N3	105.82(18)
Cd1-N6	2.208(5)	N8-Cd1-N3	91.80(17)
Cd1-N8	2.279(5)	N5-Cd1-N3	143.88(17)
		N6-Cd1-N1	168.01(18)
		N8-Cd1-N1	96.77(19)
		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)

5(A).4.4. 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. 5(A).3(a). 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. 5(A).3(b) 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. 5(A).3(c) 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



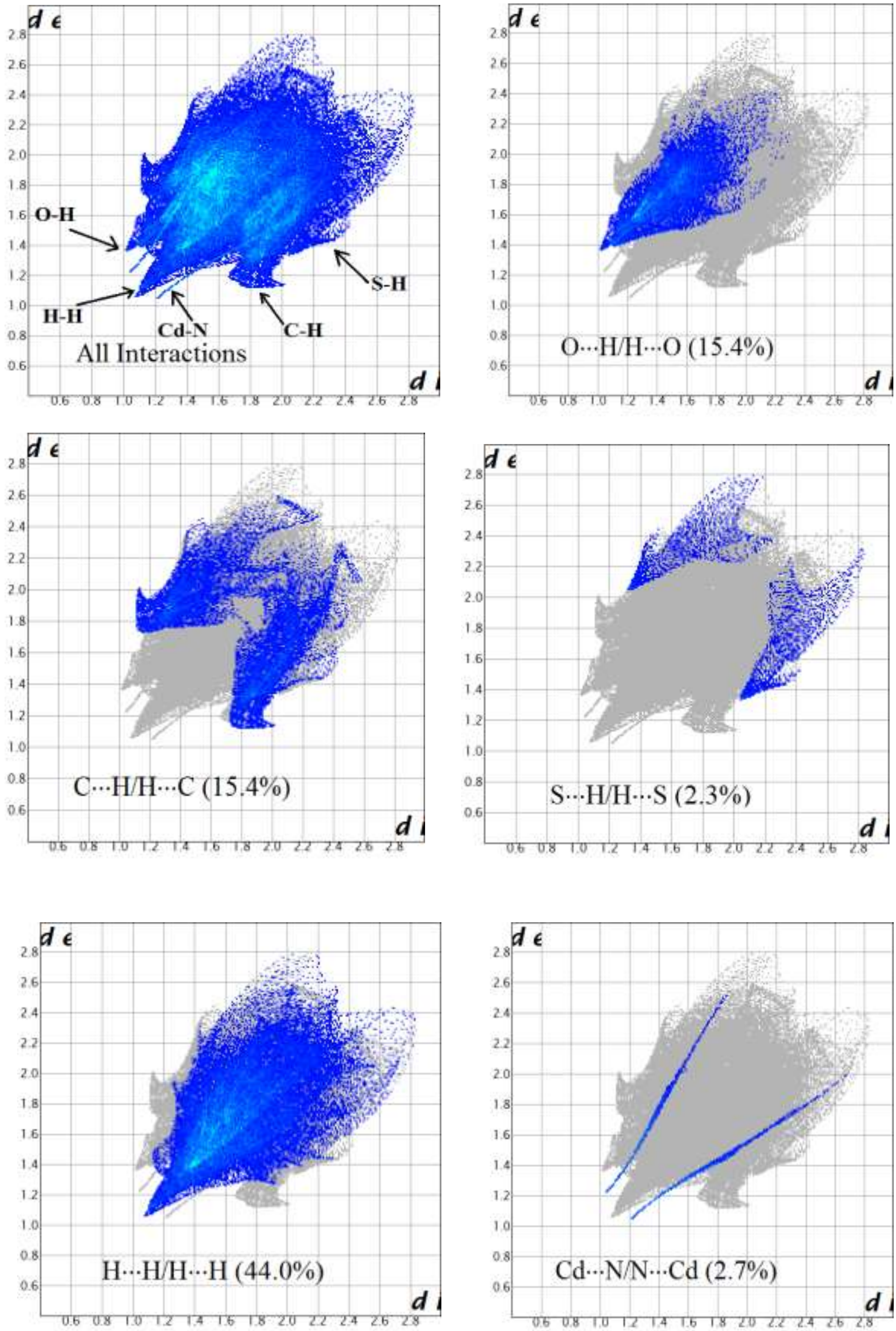
(a) **(b)** **(c)**



(d)

Figure. 5(A). 3: Hirshfeld surfaces mapped for (a) d_{norm} surfaces, (b) shape index, (c) curvature, (d) the intermolecular interactions in the polymeric Cd(II) complex.

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. 5(A).3(d). The two dimensional(2D) fingerprint plots from Hirshfeld surface analyses of the title compound is shown in. [Fig. 5(A).4] 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 FP plots also reveal the information regarding the intermolecular interaction with individual 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.


O-H
H-H
Cd-N
C-H
S-H
All Interactions
O···H/H···O (15.4%)
C···H/H···C (15.4%)
S···H/H···S (2.3%)
H···H/H···H (44.0%)
Cd···N/N···Cd (2.7%)

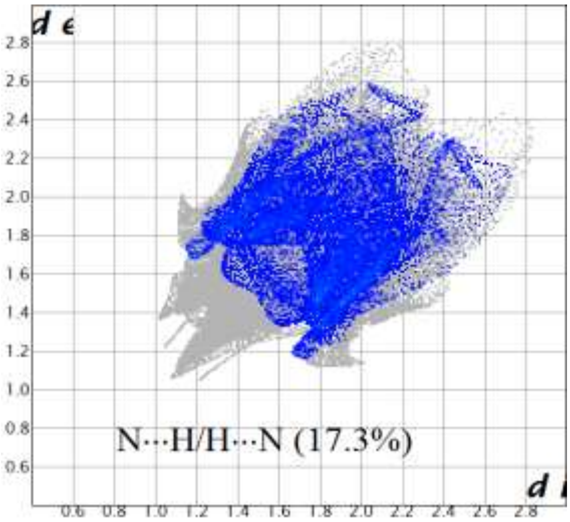


Figure. 5(A). 4. Relative contributions to the percentage of Hirshfeld surface area for the various intermolecular contacts in title compound

Table 5(A).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

All the atom---atom contacts with their relative contribution is summarized in [Table 5(A).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.

5(A).5. Conclusion

One new polymeric cadmium(II) complex $\{[Cd(bdmpe)\{N(CN)_2\}]ClO_4.CH_3OH\}_n$ has been synthesized and characterized with structure. Structural data shows each cadmium centre is bonded by two nitrile group of the μ-$_{1,5}$ dca ligand and N_3S ligand bdmpe acts as blocking ligand. Each unit cell contains non bonded one 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.

5(A).6. References

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CHAPTER-5(B)

Synthesis and Characterization of Binuclear double end-to-end dicyanamide bridged complexes of Nickel (II) and Cadmium (II) using N_4-donor pyrazole containing ligand.

Abstract

Binuclear transition metal complexes $[M(dbdmp)(\mu\text{-}_{1,5}dca)]_2(ClO_4)_2$ [M = Ni(II) and Cd(II) and dca [dca = dicyanamide anion, $N(CN)_2^-$] have been synthesized using tetradentate N_4- coordinate ligand N,N-diethyl-N′,N′-bis((3,5-dimethyl-1H-pyrazol-1-yl)methyl)ethane-1,2-diamine (dbdmp) and bridging ligand dca and characterized by spectroscopic techniques. Structural characterization by single crystal X-ray diffraction studies shows nickel(II) complex is binuclear, each nickel centre has octahedral geometry with NiN_6 coordination environment and two nickel centres are bridged by two dca ligands with $\mu\text{-}_{1,5}$ dca coordination mode.

5(B).1. Introduction

There are many reports on the syntheses, structures and magnetic properties of multinuclear transition metal complexes with pseudohalide containing bridging ligands such as azide, cyanide and thiocyanate etc [1-10]. However, the larger bridging ligand such as dicyanamide (dca) has attracted recently due to their long-range magnetic interactions in the polynuclear complexes [11-17]. The number of dca containing polynuclear complexes reported in the literature is less as compare to the other pseudohalides such as azide or thiocyanate. The important feature of the dca ligand is that it can co-ordinate to the metal centres both as terminal as well as bridging ligand. As a bridging ligand, dicyanamide ion shows different modes of coordination with transition metal ions and as a result it can produce compounds with different nuclearities [18]. When dca acts as a monodendate ligand, it forms mononuclear complex but as a bridging ligand, it can bridge a pair of metal centres either in end-to-end or end-on co-ordination mode and form single or double bridged di- or multinuclear complexes.

As our interest was to synthesis and structural characterization of polymeric transition metal complexes using dca as bridging ligand, we have reported here the syntheses and characterization of binuclear double dca bridged complexes of the type $[M(dbdmp)(\mu_{1,5}\text{-dca})]_2(ClO_4)_2$ [M= Ni(II) and Cd(II)] using tetradendate N_4-co-ordinate ligand N,N-bis(3,5-dimethyl-1H-pyrazol-1-yl)-N′,N′-diethylethane-1,2-diamine(dbdmp).

5(B).2. Experimental

5(B).2.1. Materials

The chemical and solvents were of analytical grade and purchased from commercial sources. Acetylacetone(GR, Loba, India), Paraformaldehyde(GR, Loba, India), N,N-diethyl ethylene-diamine (Aldrich) and sodium dicyanamide (Aldrich) were reagent grade and used as received. 1-hydroxymethyl-3,5-dimethylpyrazole was synthesized according to the reported method [19]. Metal perchlorate hexahydrate were prepared by the reaction of metal [Ni(II) and Cd(II)] carbonates with dilute $HClO_4$ acid and followed by evaporation of the solution on steam bath.

5(B).2.2. Synthesis of Ligand

5(B).2.2.1. Synthesis of N,N-diethyl-N',N'-bis((3,5-dimethyl-1H-pyrazol-1-yl)methyl) ethane- 1,2-diamine (dbdmp)

Ligand N,N-diethyl-N',N'-bis((3,5-dimethyl-1H-pyrazol-1-yl)methyl)ethane-1,2-diamine (dbdmp) was synthesized as per the published procedures [20].
^{1}H NMR (400 MHz, $CDCl_3$, 20ºC), δ/ppm: 0.919–0.955 (t, 6H, $–CH_2–CH_3$), 2.188–2.194 (s, 12H, 4 $–CH_3$ of pz), 2.312–2.349 (t, 2H, $–CH_2$ of ethylene diamine), 2.397–2.432 (q, 4H, $–CH_2–CH_3$), 2.734–2.771 (t, 2H, $–CH_2$ of ethylene diamine), 4.918 (s, 4H, N–CH2–N), 5.822 (s, 2H, –CH of pz ring).

5(B).2.3. Syntheses of complexes

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

5(B).2.3.1. $[Ni(dbdmp)(\mu_{1,5}\ dca)]_2(ClO_4)_2$ (1)

A methanol solution (10ml) of nickel(II) perchlorate hexahydrate (0.091g, 0.25 mmol) was added to the methanol solution (10ml) of ligand dbdmp (0.083g, 0.25mmol) slowly. The colour of the solution changed to light green and the mixture was stirred at room temperature for additional 10 min. A solution of dicyanamide(dca) (0.025g, 0.25mmol) in methanol (10ml) was added to the mixture and the colour of the solution becomes dark green immediately and the solution was stirred for additional 4h. Filtered the solution and the filtrate was kept for slow evaporation at room temperature. Green crystals were obtained after five days, filtered, washed with methanol and dried at room temperature.
Yield. 0.177g (77%). Found C = 43.35, H = 5.60, N = 16.29%. Elemental analysis calc. for $C_{40}H_{64}N_{13}O_8Cl_2Ni_2$: C= 43.16, H = 5.75, N = 16.36 %. IR (KBr pellet) cm^{-1}: νs(C≡N), 2201s, νas (C≡N), 2252 and νs+νas (C≡N), 2315; ν(C=C); ν(C=C)+ν(C=N)/pz ring, 1555 s, 1472 s; $\nu(ClO_4^-)$, 1103br; δ(O-Cl-O), 623s. UV-Vis spectra: $\lambda max(CH_3CN)$/nm (ε_{max}/mol^{-1} cm^{-1}). 616(48), 380(198), 275(399), 228(1090). $\Lambda_M(CH_3CN)(\Omega^{-1}cm^2\ mol^{-1})$ = 120. μeff = 2.75 BM.

5(B).2.3.2. $[Cd(dbdmp)(\mu\text{-}_{1,5}dca)]_2(ClO_4)_2$ (2)

A methanol solution (10ml) of cadmium(II) perchlorate hexahydrate (0.105g, 0.25mmol) was added to the methanol solution (10ml) of ligand dbdmp (0.083g, 0.25mmol). After addition the colour of the solution changed to very light yellow colour. A solution of dicyanamide (dca) (0.022g, 0.25mmol) in methanol (10ml) was added to the mixture after 10 min and the colour of the solution changed into light yellow immediately and the solution was stirred for additional 1 hr. Filtered the solution and the filtrate was kept for slow evaporation at room temperature. White crystalline compound obtained after one week, filtered and washed with methanol and dried at room temperature.

Yield. 0.100g (69%). Found C = 47.35, H = 6.32, N = 24.49%. Elemental analysis calc for $C_{40}H_{64}N_{13}O_8Cl_2Cd_2$: C = 47.51, H = 6.27, N = 24.70%. ^{1}H NMR (400 MHz, $CDCl_3$, 20^{o}C), δ/ppm: 0.786–0.879 (d, 5H, $–CH_2–CH_3$), 2.028 (s, 12H, 4 $–CH_3$ of pz), 2.103-2.373 (q, 4H, $–CH_2$ of ethylene diamine) 4.774 (s, 4H, $N–CH_2–N$), 5.653 (s, 2H, –CH of pz ring). IR (KBr pellet) cm^{-1}: νs(C≡N), 2183s, νas(C≡N)s, 2249 and νs+νas(C≡N)s, 2320; ν(C=C); ν(C=C)+ν(C=N)/pz ring, 1556 s, 1452 s; ν(ClO_4^-), 1044br; δ(O-Cl-O), 620s. UV-Vis spectra: λmax(CH_3CN)/nm (ε_{max}/mol^{-1} cm^{-1}). 388(110), 278(132), 240(553). Λ_M (CH_3CN) (Ω^{-1}cm^2 mol^{-1}) = 118.

5(B).2.4. Physical Measurements

The IR spectra of the ligand and the complexes were recorded on a Bruker Alpha spectrometer using KBr pellets. The micro analyses (C, H and N) were carried out using a Thermo Finnigan Flash EA 1112 series elemental analyzer. UV-Vis spectra (900 - 190 nm) of the ligand and complexes were recorded on a JASCO V-730 in CH_3CN solution (1×10^{-3} M). Equip-Tronics conductivity meter (model no. EQ660 A) was utilized to measure solution conductivity in acetonitrile solution (1×10^{-3} M). Room temperature magnetic susceptibilities of powder samples were measured using Guoy balance.

5(B).3. X-ray Crystallography

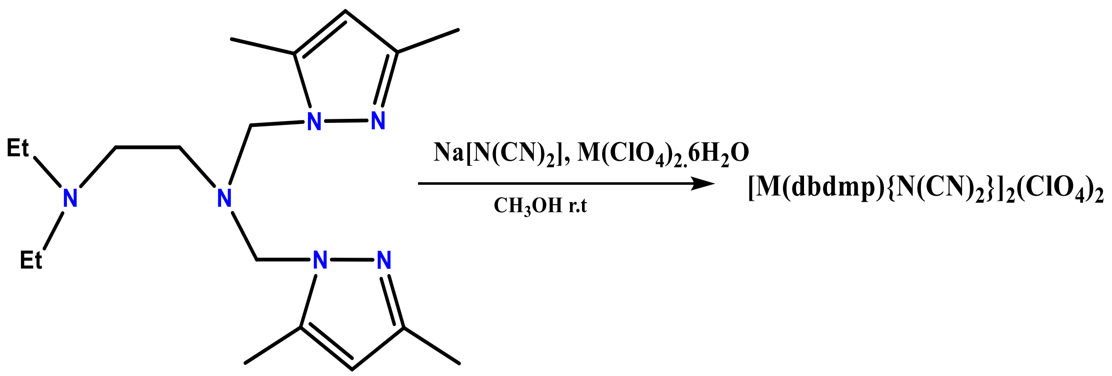
The summary of data collection and structure refinement parameters for the complex **1** is given in Table 5(B).1 and selected bond lengths (Å) and angles (º) are given in Table 5(B).2. Suitable single crystal was placed in viscous oil, carefully selected under polarizing microscope and mounted on a glass fiber. Accurate unit cell parameters were determined by least squares fit of 2θ values and reflection intensity data collected on Oxford X-CALIBUR-S diffractometer equipped with Cu-Kα radiation (λ = 1.54184 Å) for the complex using the ω technique at 293 K. The data interpretations were processed with CrysAlisPro, Agilent

Technologies, Version 1.171.35.19 [21]. An absorption correction based on multi-scan method was applied [22]. 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 [23].
All calculations were carried out using WinGX system Ver-1.64 [24]. All non-hydrogen atoms were refined anisotropically. The positions of the hydrogen atoms were calculated from the difference Fourier map, placed in the calculated positions. ORTEP3 Windows program were used for generating for molecular graphics [25].

5(B).4. Results and discussion

5(B).4.1. Syntheses

The ligand N,N-bis(3,5-dimethyl-1H-pyrazol-1-yl)-N′,N′-diethylethane-1,2-diamine (dbdmp) was synthesized as a yellow viscous liquid by the reaction between N-(3,5-dimethyl-1H-pyrazole-1-yl)methanol and N,N- diethylethylenediamine in acetonitrile as per reported method [20]. The ligand was characterized by ^{1}H NMR. The ligand possesses four potential donor sites- two nitrogen donor atoms from two pyrazole ring and two nitrogen atoms from the tertiary amine.



Scheme 5(B). 1. Syntheses of the complexes [M = Ni and Cd)

The complexes of Ni(II) and Cd(II) were synthesized by stirring the appropriate metal perchlorate hexahydrate, ligand N-bis(3,5-dimethyl-1H-pyrazol-1-yl)-N′,N′-diethylethane-1,2-diamine (dbdmp) and dca in 1:1:1 mole ratio at room temperature in methanol [scheme 5(B).1].

Table 5(B).1 Crystal parameters of Ni(II) complex

	[Ni(dbdmp)($\mu_{1,5}$-dca)]$_2$(ClO_4)$_2$
Empirical formula	$C_{40}H_{64}N_{18}Ni_2O_{10}Cl_2$
Formula weight	556.68
Temperature/K	293
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	10.2458(8)
b/Å	15.9765(11)
c/Å	16.0331(13)
α/°	90
β/°	94.338(8)
γ/°	90
Volume/Å^3	2617.0(3)
Z	4
ρ_{calc}g/cm^3	1.4128
μ/mm^{-1}	0.887
F(000)	1170.4
Crystal size/mm^3	0.3 × 0.2 × 0.2
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	5.7 to 58.62
Index ranges	$-14 \le h \le 13$, $-21 \le k \le 21$, $-22 \le l \le 21$
Reflections collected	56323
Independent reflections	6629 [R_{int} = 0.1052, R_{sigma} = 0.0805]
Data/restraints/parameters	6629/0/322
Goodness-of-fit on F^2	1.080
Final R indexes [I>=2σ (I)]	R_1 = 0.0797, wR_2 = 0.1633
Final R indexes [all data]	R_1 = 0.1363, wR_2 = 0.1861
Largest diff. peak/hole / e Å^{-3}	1.22/-0.85

CCDC number.	2048747

There was no change of molecular structure of the complexes when excess mole ratio of dca used in the synthesis. Diffraction quality crystal of Ni(II) complex for X-ray diffraction studies were obtained by slow evaporation of the solution. We are unable to obtain diffraction quality crystal for Cd(II) complex even after several attempts. The molecular composition of the complexes was determined by the IR, molar conductivity measurement and single crystal diffraction studies. Molar conductivity measurement in CH_3CN indicates the complexes are 1:1 electrolyte. Single crystal X-ray diffraction studies showed that the Ni(II) complex is binuclear with octahedral geometry. All the complexes are soluble in DMF, DMSO, acetonitrile but insoluble in organic solvents such as methanol, dichloromethane etc.

5(B).4.2. Spectral Data

5(B).4.2.1. ^{1}H NMR and ESI-Mass spectral data

The ^{1}H NMR spectrum of Cd(II) complex [Fig.5(B).1] shows peak at 2.028 δ ppm which confirm the presence of four methyl group of pyrazole ring. The doublet appear at 0.786-0.879 ppm confirms the presence of CH_2-CH_3 group of two ethyl group of ethylenediamine. One quarter appear at 2.103-2373 ppm confirmed the presence of CH_2-CH_2 of ethylenediamine moiety and a singlet appeared at 4.774 ppm confirming the presence of -CH_2- which is connected with pyrazole and ethylenediamine moiety. The aromatic protons of pyrazole ring appeared at 5.653 ppm

ESI mass spectrum of Cd(II) complex showed peak at m/z 509.6($(C_{20}H_{32}N_9Cd)^+$. This value is compatible with the theoretical molecular weights. The spectrum displayed multiple peaks corresponding to successive degradation of the formation of different fragments appeared at m/z 333 and 445 corresponding to $[C_{18}H_{32}N_6]^+$and $[C_{18}H_{32}N_6Cd]^+$, respectively as shown in [Figure 5(B).2].

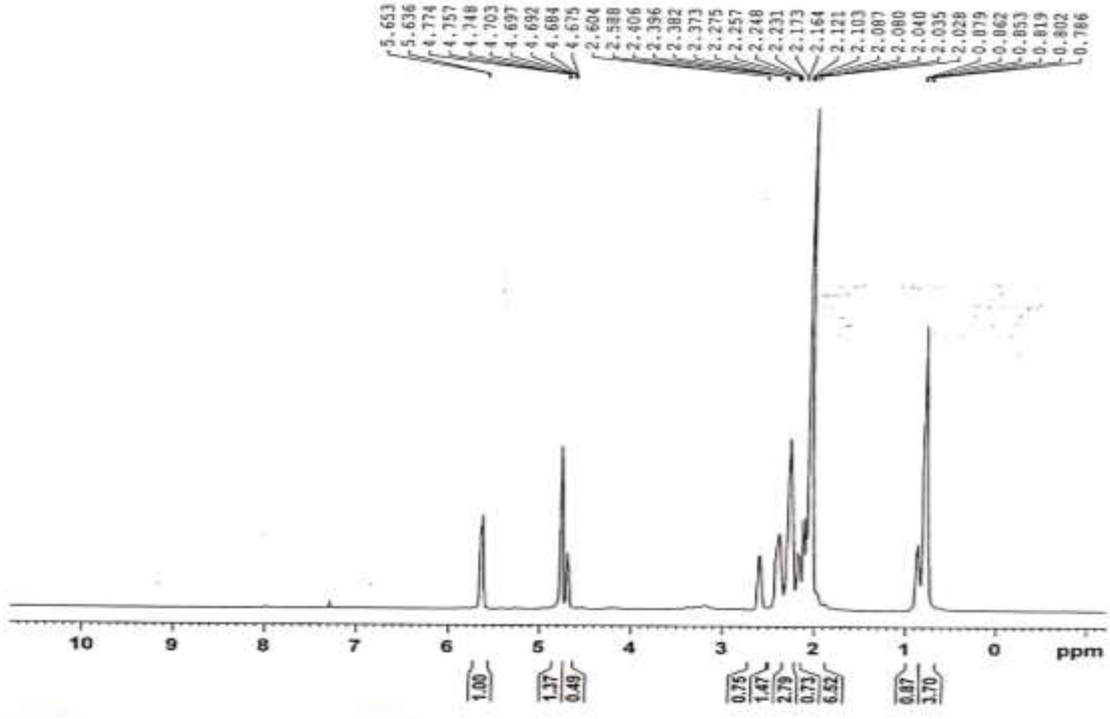


Figure 5(B).1. ^{1}H NMR spectrum of $[Cd(dbdmp)(\mu_{1,5}\text{-dca})]_2(ClO_4)_2$

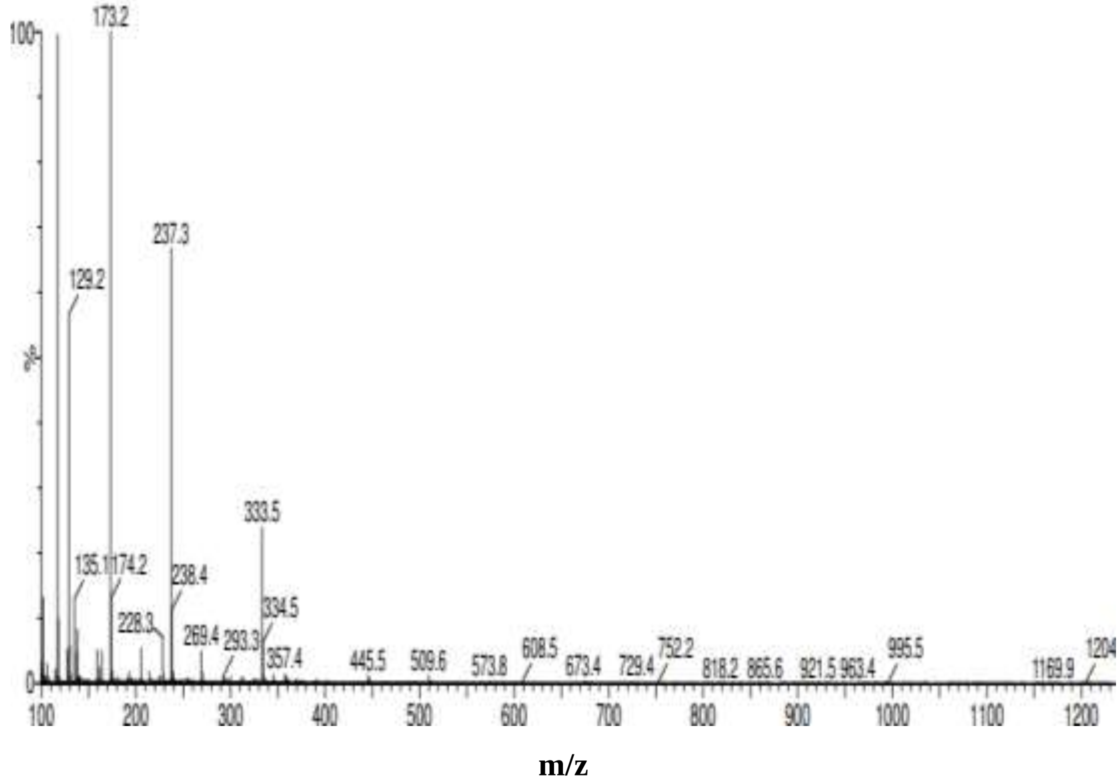


Figure 5(B).2. ESI-Mass spectrum of $[Cd(dbdmp)(\mu_{1,5}\text{-dca})]_2(ClO_4)_2$

5(B).4.2.2. IR spectral data

The IR spectra of the complexes were assigned in comparison to the s of the ligand dbdmp. Both the complexes show two intense bands at ~1555 and ~1472 cm^{-1} and these two bands are also present in the ligand, indicating the coordination of the ligand dbdmp in the metal complexes. A series of three strong bands appeared in the region of 2183–2320 cm^{-1} due to ν(C=N) for the complexes which are assigned as ν(C=N). One strong band at 2183 cm^{-1} due to νs(C≡N) and two weak bands- one at 2250 cm^{-1} due to νas(C≡N) and at 2320 cm^{-1} due to νs+νas(C≡N) of bridging dca ligand in the complexes. The IR spectra of complexes exhibited a broad band at ~1100 cm^{-1} due to ν(Cl–O) and a weak band at ~623 cm^{-1} due to δ(O–Cl–O), confirming the presence of the perchlorate ion outside the coordination sphere in the complexes.

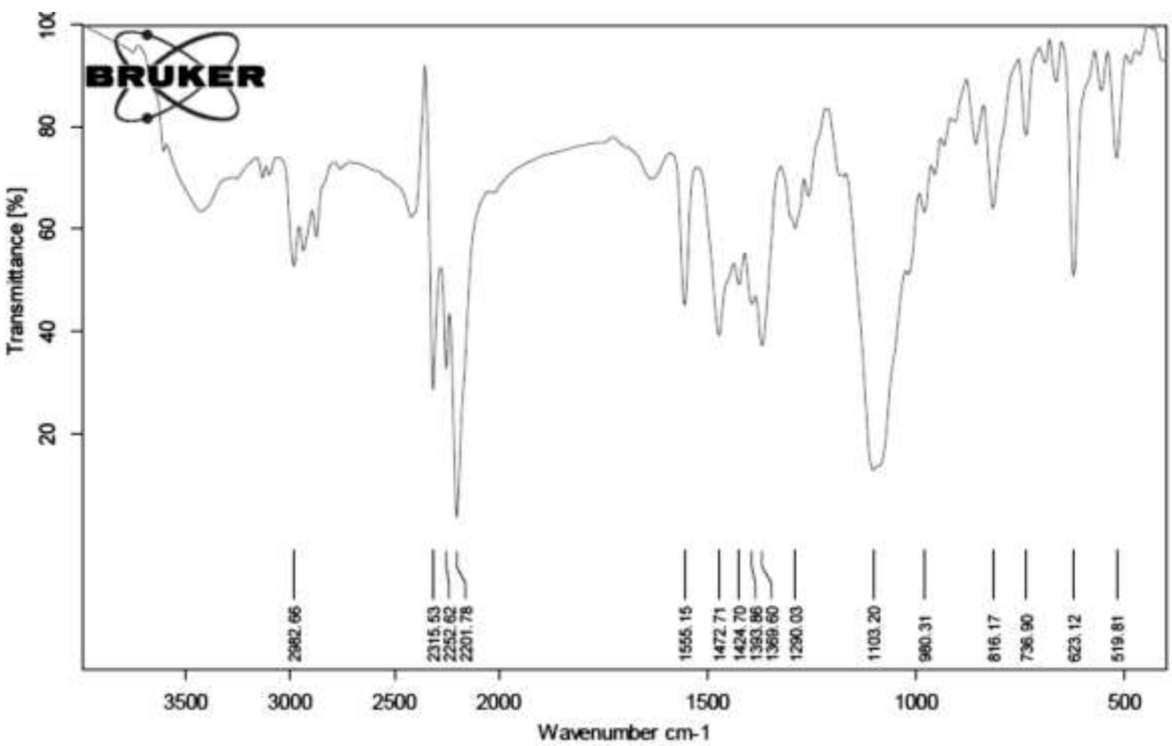


Figure 5(B).3. IR spectrum of $[Ni(dbdmp)(\mu_{1,5}\text{-}dca)]_2(ClO_4)_2$

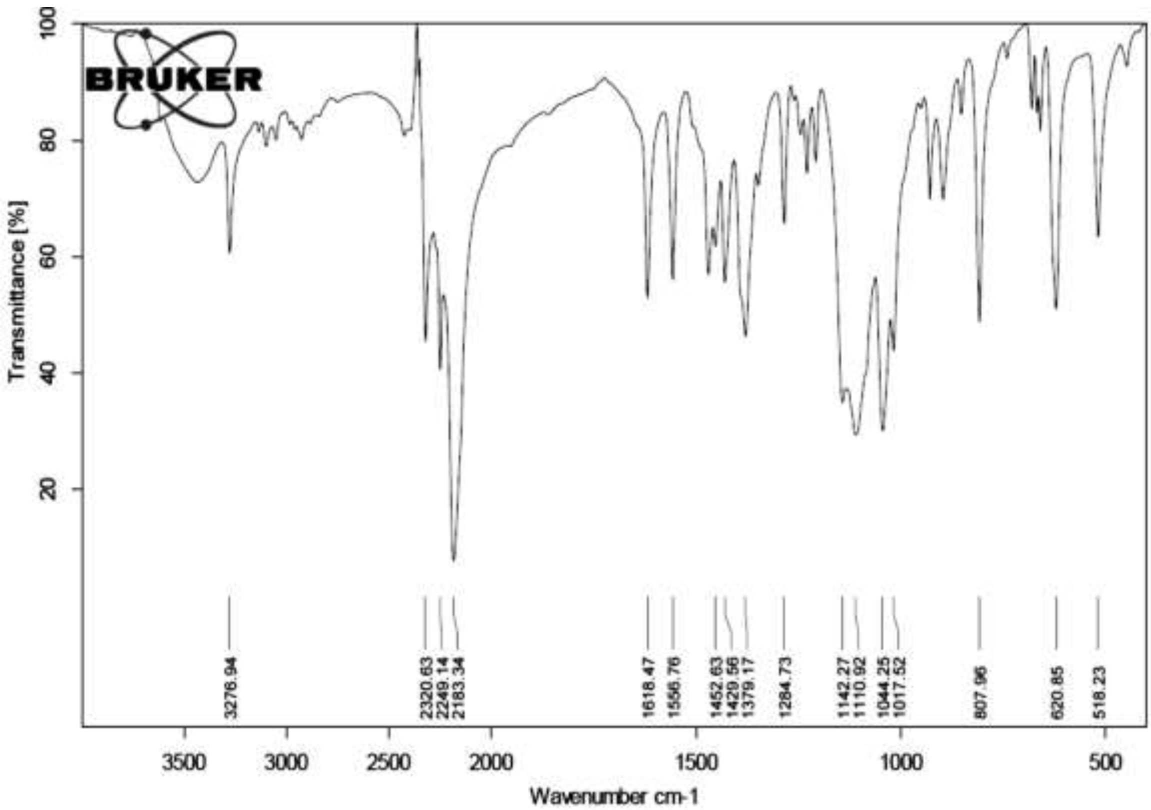


Figure 5(B).4. IR spectrum of $[Cd(dbdmp)(\mu_{1,5}\text{-}dca)]_2(ClO_4)_2$

5(B).4.2.3. Electronic Spectra and magnetic studies.

The UV-Visible spectra of both the complexes were recorded in CH_3CN (10^{-3}M) in the range of 200-900 nm. The high intensity bands appeared at < 400nm are due to intra ligand n-π* and π - π * charge transfer transition. In the visible region, one absorption band was observed at 616 nm with low molar absorption coefficient for Ni(II) complex and this is due to d-d transition.

Room temperature magnetic susceptibility measurement of the complex **1** shows the μ_{eff} value is 2.75 BM indicating two electrons paramagnetism with octahedral geometry. As the distance between Ni---Ni in the complex is 7.270Å, we have not studied variable temperature magnetic study of this complex as most of the reported complexes show very weak interaction [26].

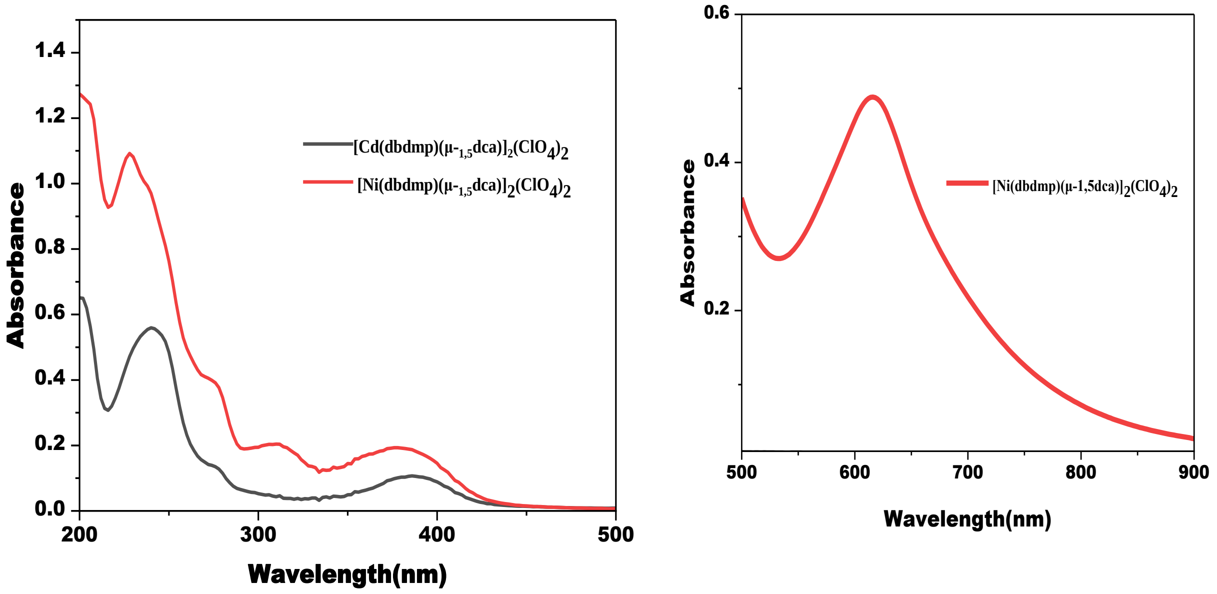


Figure 5(B).5. Electronic spectra of complexes in CH_3CN (10^{-3} M).

5(B).4.3. Description of Crystal Structure

5(B).4.3.1. Structure of $[Ni(dbdmp)(\mu\text{-}_{1,5}dca)]_2(ClO_4)_2$

Single crystal X-ray data shows it is binuclear nickel(II) compound bridged by two μ-$_{1,5}$dca between two nickel centres. Each nickel centre has N_6 coordination environment and surrounded by nitrogen atoms N1, N6, N2 and N4 of the ligand dbdmp and two nitrogen atoms N7 and N9 from nitrile groups of the μ-$_{1,5}$-dca molecules. In the equatorial plane there are four nitrogen atoms N2, N4, N9 and N7 and N1 and N6 are in the axial position. The equatorial bond distances Ni-N2 (2.101Å), Ni-N4(2.084Å), Ni-N9 (2.101Å) and Ni-N7 (2.034Å) are nearly equal whereas axial bond distances Ni-N1 (2.269Å) and Ni-N6 (2.111Å) are different. Two axial bond angles N4-Ni-N9(174.53^0) and N7-Ni-N2 (176.88^0) are close to 180^0. The axial bond angle N6-Ni1-N1 (161.70^0) is not linear (180^0) which produce distortion in the molecule. Two nickel centres are joined through Ni1-N9-C32-N8-C34-N7-Ni1 and the distances are Ni-N9 (2.033 Å), N9-C32 (1.139 Å), C32-N8 (1.304Å), N8-C34 (1.302 Å), C34-N7(1.148 Å) and Ni-N7 (2.033 Å). The bridging dca between the two nickel centres is not linear but angular (V shape) which was proved through bond angle of C32-N8-C34 is 121.05. The double dca produce 12 members ring with two Ni(II) centres. The Ni----Ni distances between the two molecules is 7.270Å.

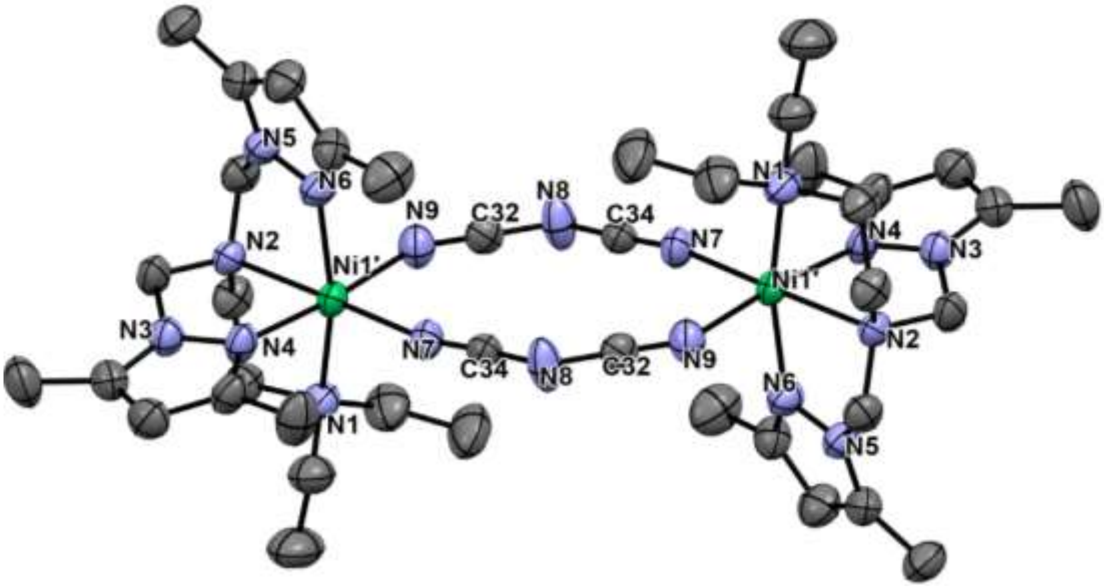


Figure. 5(B).6. Crystal structure of [Ni(dbdmp)(μ-1,5dca)]$_2$(ClO$_4$)$_2$]. H-atoms and perchlorate ions are omitted for clarity.

Table 5(B).2 Bond lengths (Å) and angles (º) of Ni(II) complex.

Bond lengths(Å)		Bond angles(º)	
Ni1 – N2	2.133(3)	N1 - Ni1 – N2	82.79(14)
Ni1 – N1	2.269(4)	N7 - Ni1 – N2	176.85(15)
Ni1 – N7	2.034(4)	N7 - Ni1 – N1	98.31(15)
Ni1 – N9	2.101(4)	N9 - Ni1 – N2	94.47(15)
Ni1 – N4	2.084(4)	N9 - Ni1 – N1	90.10(16)
Ni1 – N6	2.111(4)	N9 - Ni1 – N7	88.49(16)
		N4 - Ni1 – N2	80.88(14)
		N4 - Ni1 - N11	92.15(15)
		N4 - Ni1 – N7	96.11(15)
		N4 - Ni1 – N9	174.53(15)
		N6 - Ni1 – N2	79.61(14)
		N6 - Ni1 - N1	161.70(14)
		N6 - Ni1 – N7	99.52(15)
		N6 - Ni1 – N9	86.30(16)
		N6 - Ni1 – 4	90.02(15)

5(B). 5. Conclusion

Two dinuclear double dca [$\{N(CN)_2\}^-$] bridged metal complexes of the type [M(dbdmp)($\mu_{1,5}$-dca)]$_2$(ClO_4)$_2$ [M= Ni(II) and Cd(II)] have been synthesized and characterized. Single crystal X-ray diffraction study of the Ni(II) complex shows it is binuclear double end-to-end dca bridged complex and the coordination mode of dca is μ-1,5 in both the complexes and this is the best coordination mode of dca during complex formation

5(B).6. References

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