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Feature article

Structural studies on Cd(II) complexes incorporating di-2-pyridyl ligand and the X-ray crystal structure of the chloroform solvated DPMNPH/CdI_2 complex

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ABSTRACT

A series of novel Cd(II) complexes incorporating ligand, di(2-pyridinyl)methanone *N*-(2-pyridinyl)hydrazone (DPMNPH), has been investigated. The ligand, DPMNPH, and its corresponding complexes have been characterized with the help of a number of techniques: microanalysis, FT-IR, ^{1}H and ^{13}C NMR, UV/vis spectroscopy, thermal studies and MS–FAB mass spectrometry. In addition, single crystal X-ray diffraction measurement studies are also employed in one of the complexes showing a distorted trigonal bipyramidal geometry. Furthermore, the existence of NH···Npy intramolecular hydrogen bonding interactions in the ligand and its corresponding complexes has also been reported.

Contents

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Introduction

Schiff bases are important class of organic ligands, and have been extensively studied in coordination chemistry due to their facile synthesis and easily tunable steric and electronic properties [1,2]. Furthermore, Schiff bases provide opportunities for inducing substrate chirality, tuning the metal centered electronic future, enhancing the solubility and stability of either homogeneous or heterogeneous catalysts [3–5]. Schiff base-transition metal complexes have been among the most widely studied coordination compounds for many years [6]. Moreover, the structural diversity leading to supramolecular architecture through various non-covalent intermolecular interactions in the solid state gives further impetus to the extensive study of these complexes [7–9]. In recent years, the coordination chemistry of N2 coordinated ligands has received a lot of attention because of their relevance to biological systems [10]. Among them, dipyridyl ligands have been extensively studied in coordination chemistry for the synthesis of transition metal complexes with magnetic properties [11,12]. Moreover, dipyridyl can bind as a monodentate or bidentate ligand, thus demonstrating the ability to form mononuclear or dinuclear complexes [13]. Furthermore, various dipyridyl ligands containing flexible bridge groups have been widely studied in coordination chemistry because of their catalytic and anticarcinogenic properties [14–16]. Due to the rigidity of these chelate rings, the conformation that they adopt can be described as boat conformation, which has been observed in some dipyridyl complexes of Au(III), Pd(II) and Cu(II) [16–18]. In recent years, hydrazones have received considerable attention because of their versatility in coordination modes, flexibility in assuming different conformations, pharmacological activity and their use in analytical methods. Furthermore, the possibility of tautomerism makes the studies of their coordination modes extremely interesting [19]. Among hydrazones, the bipyridylhydrazones were found to function as chelating ligands for many transition metal ions [20,21]. Complexes of d^{10} metal ions, such as zinc(II) and cadmium(II) are also of great interest because of their involvement in various biological processes [22]. The chemical similarity of zinc(II) and cadmium(II) suggests that the latter may displace the former from the active site in enzymes containing zinc(II) [23]. The cadmium(II) ion has recently been found to serve as the catalytic center in a newly discovered carbonic anhydrase [24]. Furthermore, cadmium(II) compounds have been very interesting in the context of their structural diversity and photophysical properties. The coordination sphere of Cd(II) is flexible with the coordination numbers ranging from four to eight, corresponding to different geometries viz., tetrahedron, square plane, square pyramid, trigonal bipyramid, octahedron, pentagonal bipyramid, bicapped triangular prism, and dodecahedron [25]. A part of our ongoing research interest is directed towards chemistry of Schiff bases and their complexes with various transition metal ions [26–29]. The variety of possible Schiff base metal complexes with wide choice of ligands and their coordination environment has prompted us to undertake research in this area. In the present study, we report the results of our investigations on the synthesis of ligand, DPMNPH, di(2-pyridinyl)methanone *N*-(2-pyridinyl)hydrazine, derived from di-2-pyridyl ketone and 2-hydrazinopyridene, and its complexes with cadmium halides. The synthesized ligand and its Cd(II) complexes have been characterized by various spectroscopic studies. The single crystal X-ray structure of DPMNPH/CdI_2 has also been determined.

Experimental

General remarks, materials and physical measurements

The starting materials, di-2-pyridyl ketone, 2-hydrazinopyridine and CdX_2 were purchased from Merck and used as received. Elemental analyses were carried out on an Elementar Varrio EL analyzer. High-resolution ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DRX 250 spectrometer at 298 K. FT-IR spectra were obtained using KBr disks (4000–400 cm^{-1}) on a Shimadzu 8300 FT-IR spectrophotometer. The electronic spectra in the 200–800 nm range were obtained on a Perkin Elmer Lambda 45 spectrophotometer and FAB-MS data were obtained on a Bruker IFS 48 FT-IR spectrometer and Finnigan 711A (8 kV), modified by AMD and reported as mass/charge (m/z), respectively.

Synthesis of di(2-pyridinyl)methanone N-(2-pyridinyl)hydrazine, DPMNPH

An ethanolic solution of di-2-pyridyl ketone (0.184 mg, 1 mmol) was added dropwise to an ethanol solution of 2-hydrazinopyridine (0.109 mg, 1 mmol). The reaction mixture was refluxed for 3 h, and allowed cooling at room temperature. After cooling, distilled water was added at a volume ratio up to 1:3 (V_{org}:V_{aq}) followed by the addition of few drops of sodium hydroxide solution to neutralize the reaction mixture. A microcrystalline solid separated out, washed with ethanol and dried in vacuum over fused $CaCl_2$.

Yield 88%, M.P. = 253 °C, color, yellow, anal. calc. C, 69.80; H, 4.76; N, 25.43% found: C, 69.56; H, 4.47; N, 25.25% ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 6.5–9.5 (m, 12H, Py's), 13.9 (s, 1H, **H**N). ^{13}C NMR ($CDCl_3$, 400 MHz): δ (ppm) 108.3–156.2 (m, 15C, Py's), 157.1 (br, 1C, C═NN), IR, (KBr, cm^{-1}), 1640 $\nu_{(C=N)}$.

Synthesis of the cadmium(II) complexes, [DPMNPH/CdX_2] [X = Cl^-, Br^-, I^-]

A methanolic solution of CdX_2 (1 mmol) was added dropwise to the solution of DPMNPH ligand (1 mmol) in the same solvent in 1:1 M molar ratio with constant stirring for 2 h. The resulting reaction mixture was concentrated to 4 ml under reduced pressure. The product of desired complex was precipitated by adding 50 ml of dry diethyl ether, which was filtered and then dried under a vacuum to obtain analytically pure compound. The resulting compound was recrystallized by slow diffusion of diethylether to the solution of DPMNPH–CdX_2 in chloroform. Crystals suitable for X-ray measurement were obtained for DPMNPH/CdI_2. No crystal was found suitable for X-ray measurement for complexes, DPMNPH/$CdCl_2$ and DPMNPH/$CdBr_2$.

DPMNPH–$CdCl_2$, yield 82%, M.P. = 370 °C, color, white, anal. calc. C, 41.90; H, 2.86; N, 15.27% found: C, 41.72; H, 2.71; N, 15.68% ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.5–9.5 (br, m, 12H, Py's), 11.4 (s, 1H, **H**N). ^{13}C NMR ($CDCl_3$, 400 MHz): δ (ppm) 111.5–156.3 (15C, Py's), 148.8 (1C, C═NN), IR (KBr, cm^{-1}), 1610 $\nu_{(C=N)}$.

DPMNPH–$CdBr_2$, yield 85%, M.P. = 395 °C, color, yellow, anal. calc. C, 35.10; H, 2.39; N, 12.79% found: C, 35.32; H, 2.28; 12.26 5% ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.5–9.5 (br, m, 12H, Py's), 11.5 (s, 1H, **H**N). ^{13}C NMR ($CDCl_3$, 400 MHz): δ (ppm) 113.1–157.1 (15C, Py's), 143.2 (1C, C═NN), IR (KBr cm^{-1}) 1630 $\nu_{(C=N)}$.

DPMNPH–CdI_2, yield 90%, M.P. = 410 °C, color, yellow, anal. calc. C, 24.62; H, 1.71; N, 7.95% found: C, 24.55; H, 1.65; N, 7.88% ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.5–9.5 (m, 12H, Py's), 11.3 (s, 1H, **H**N). ^{13}C NMR ($CDCl_3$, 400 MHz): δ (ppm) 110.1–155.4 (15C, Py's), 144.4 (1C, C = NN), IR (KBr cm^{-1}) 1620 $\nu_{(C=N)}$.

X-ray structural analyses for the DPMNPH–CdI_2 complex

Data for DPMNPH–CdI_2 complex were collected at 173(2) Siemens P4 diffractometer operating in the omega scan mode, using graphite monochromated Mo Kα radiation (λ = 0.71073°A). Details of crystal data, data collection, and structure refinement are given in Table 1. The structure was solved by direct methods using the Bruker SHELXS-97 program and refined by full matrix least-squares on F^2 using the Bruker SHELXL-97 program [30].

Results and discussion

The synthesis of building components, di-2-pyridylketone and 2-hydrazinopyridine in 1:1 molar ratio in ethanol led to the formation

Table 1
Crystal data and structure refinement for DPMNPH–CdI_2.

Empirical formula	$C_{16}H_{13}CdI_2N_5$, 2($CHCl_3$)	
Formula weight	880.26	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.0678(11) Å	α = 116.9730(10)°
	b = 12.1683(13) Å	β = 91.159(2)°
	c = 12.6851(14) Å	γ = 103.296(2)°
Volume	1333.9(3) $Å^3$	
Z	2	
Density (calculated)	2.192 Mg/m^3	
Absorption coefficient	3.752 mm^{-1}	
F(000)	828	
Crystal size	0.20 × 0.15 × 0.10 mm^3	
Theta range for data collection	1.82 to 28.28°	
Index ranges	$-13 \le h \le 13$, $-16 \le k \le 14$, $0 \le l \le 16$	
Reflections collected	25,603	
Independent reflections	6581 [R(int) = 0.0515]	
Completeness to theta = 28.28°	99.2%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.6656 and 0.5647	
Refinement method	Full-matrix least-squares on F2	
Data/restraints/parameters	6581/0/293	
Goodness-of-fit on F2	1.067	
Final R indices [I > 2sigma(I)]	R1 = 0.0331, wR2 = 0.0612	
R indices (all data)	R1 = 0.0517, wR2 = 0.0671	
Largest diff. peak and hole	1.616 and −0.961 e.$Å^{-3}$	

of di(2-pyridinyl)methanone *N*-(2-pyridinyl)hydrazone (DPMNPH) ligand in good yield. The synthesized ligand served as a polydentate chelating ligand towards CdX_2 (X = Cl^-, Br^- and I^-), and revealed the formation of neutral mononuclear DPMNPH–CdX_2 complexes (Scheme 1). The formed complexes were stable in air and soluble in common organic solvents. Elemental analysis studies for the DPMNPH free ligand and its CdX_2 complexes were in a good agreement with their proposed composition formula of the desired complexes.

Mass spectra

The FAB-MS spectrum of the DPMNPH free ligand showed a molecular ion peak ($[M]^+$, 100%) (m/z) at 275.1, calc. 275.8 belongs to the formula $C_{16}H_{13}N_5$. In the spectra of the complexes, FAB-MS molecular ion peak of DPMNPH–$CdCl_2$ complex appearing at (m/z) 458.9, calc. 458.6 belongs to the formula $C_{16}H_{13}CdCl_2N_5$. The molecular ion peak of DPMNPH–$CdBr_2$ complex appearing at (m/z) 546.9, calc. 547.5 belongs to the formula $C_{16}H_{13}Br_2CdN5$. The molecular ion peak of DPMNPH–CdI_2 complex appearing at (m/z) 779.8, calc. 880.2 belongs to the formula $C_{16}H_{13}I_2CdN_5$.

NMR investigations

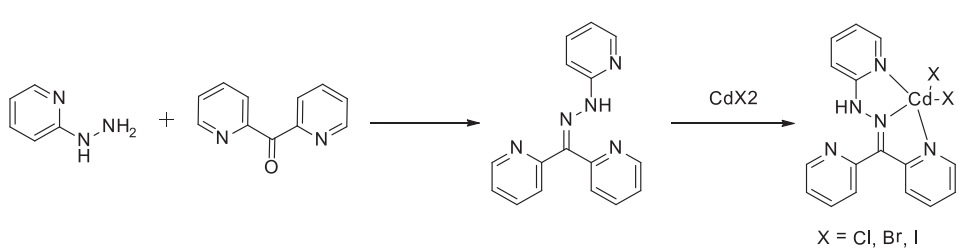
The ^1H and ^{13}C NMR spectra of the DPMNPH free ligand and its CdX_2 complexes were recorded in $CDCl_3$, and the spectral data are given in experimental part. N – H proton is shown as a singlet and appeared at 13.9 ppm in the free DPMNPH ligand. Pyridine ring protons are shown as multiplets at 6.5–9.0 ppm range in free ligand (Fig. 1S(a)). The spectra of DPMNPH–CdX_2 complexes show upfield shift in NH proton and appear at ~11.8 ppm. There is a little change in the shift of pyridyl ring protons and appear at 7.0–9.0 ppm range (Fig. 1S(b)). The ^{13}C NMR spectrum of ligand, DPMNPH shows a sharp resonance signal at 145.8 ppm attributed to C═N carbon atom. The pyridyl ring carbons are shown at 108.2–157.1 ppm range (Fig. 2S). Upon complexation, C═N carbon atoms are shifted to the lower regions ~143.4 ppm compared to free ligand, confirming the coordination of C═N to Cd(II) ions, while the pyridyl ring carbon atoms are shown at 120–160 ppm range.

Electronic absorption spectral studies

Electronic spectra of ligand, DPMNPH and its DPMNPH–CdX_2 complexes were measured in chloroform (Fig. 3S). The electronic spectrum of free ligand shows a strong band at 290 nm due to π–π* of aromatic ring [1]. The absorption bands observed at 355 nm may be assigned to *n*–π* transition associated with C═N linkages [31]. Upon complexation, the position of these bands shifted and appears at 368 nm, 390 nm, and 390 nm for DPMNPH–$CdCl_2$, DPMNPH–$CdBr_2$ and DPMNPH–CdI_2, respectively suggesting the coordination of iminic nitrogen to Cd(II) ion [32,33]. The bands observed at 478 nm, 620 nm and 570 nm for DPMNPH–$CdCl_2$, DPMNPH–$CdBr_2$ and DPMNPH–CdI_2 complexes may be assigned to charge transfer L–M bands [1].

IR spectral investigations

A comparative study of IR spectral data of the reported complexes with that of the free ligand gives sufficient evidences towards the better understanding of the coordinating behavior of the ligand, DPMNPH (Fig. 4S). The absorption band due to $\nu_{(C=N)}$ observed at 1640 cm^{-1} in the free ligand is shifted to lower wave number and appeared at 1610 cm^{-1}, 1630 cm^{-1} and 1620 cm^{-1} for DPMNPH–$CdCl_2$, DPMNPH–$CdBr_2$ and DPMNPH–CdI_2 complexes, respectively, indicating the coordination of Cd(II) ion to iminic nitrogen of $\nu_{(C=N)}$ group, consistent with the presence of bands at ~570–620 cm^{-1} for all the complexes, attributed to $\nu_{(N-Cd)}$ vibrations [34,35]. Interestingly, the sharp band due to $\nu_{(N-H)}$ (~3380–3300 cm^{-1}) is absent in free ligand and its all in the complexes. Instead, it appeared as broad peak in FT-IR spectra of the free ligand and its corresponding complexes (Fig. 4S). Furthermore, it was also supported



Scheme 1. Schematic representation of preparation of DPMNPH ligand and DPMNPH/CdX_2 complexes.

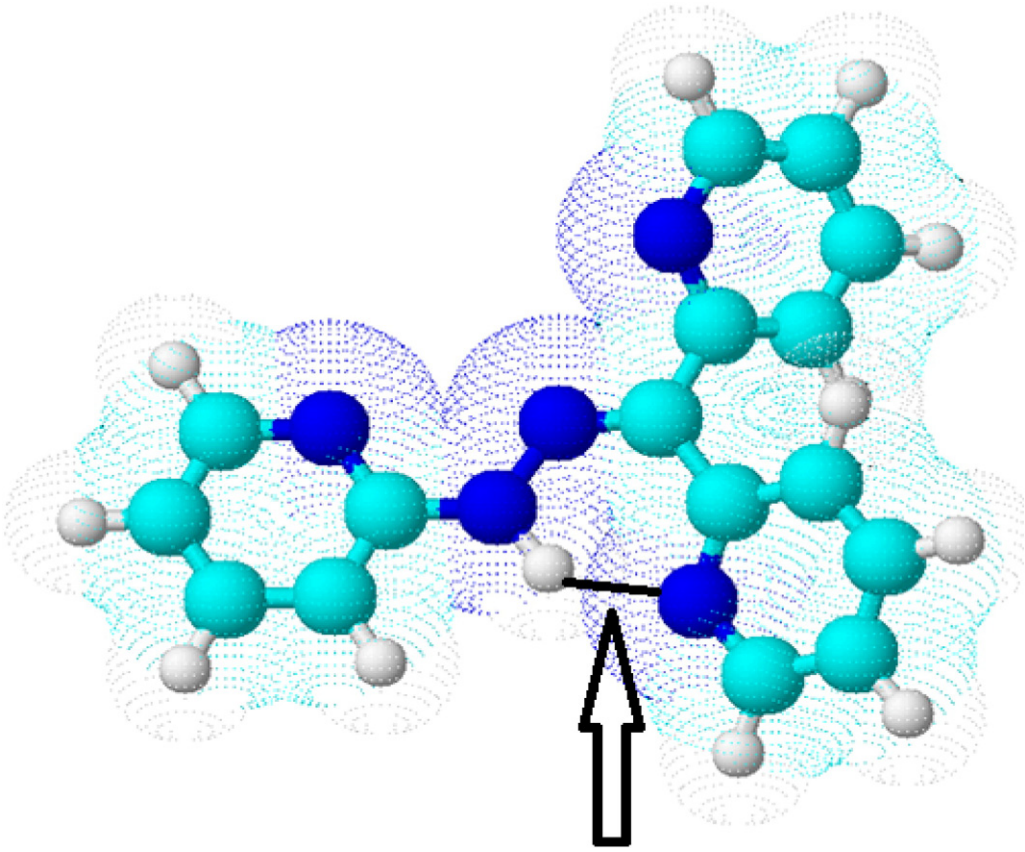


Fig. 1. Optimization structure of the free ligand with N – H···Py intramolecular hydrogen bond stabilized by six membered ring formation.

by X-ray crystal structure showing the intramolecular-hydrogen bond between N – H and the one in which the N-pyridine belongs to the ketone (N – H···NPy) (Fig. 1) [21]. Unfortunately, we don't have good crystals of the free ligand suitable for X-ray single crystal measurement to support the formation of N – H···Py intramolecular-hydrogen bond in the ligand. The bands appeared at 3200–3100 cm^{-1} and 1620–1600 cm^{-1} are

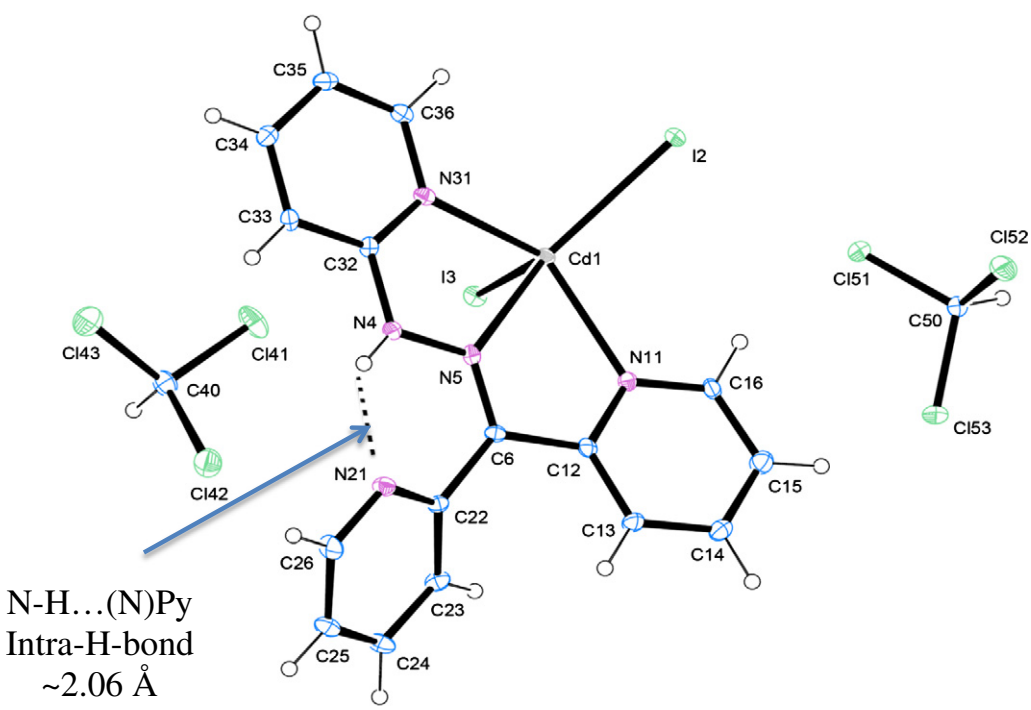


Fig. 2. Molecular structure of the DPMNPH–CdI_2 complex with atom labeling. Thermal ellipsoids are drawn at the 50% probability level.

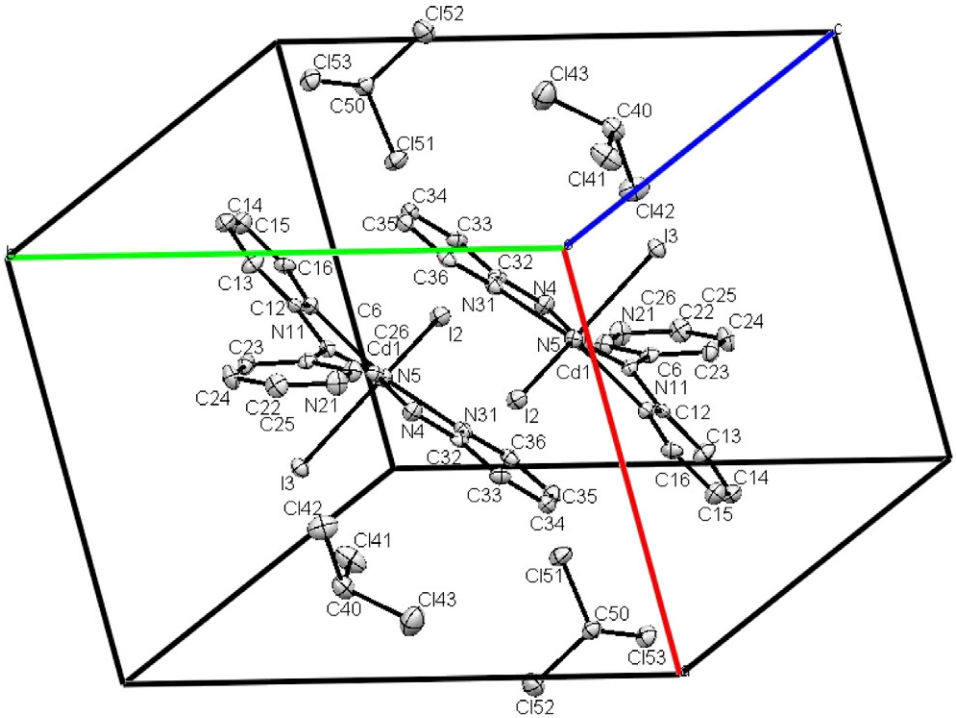


Fig. 3. A view of packing the DPMNPH–CdI_2 complex chains extending along a-axis.

assigned to $\nu_{(H-C)}$, $\nu_{(C=C)}$ of aromatic vibrations, while the other bands were found at their expected positions.

Thermogravimetric analyses

The thermal stabilities of the complexes were investigated by TG/DTA. The TG/DTA curves were obtained at a heating rate of 10 °C min^{-1} in air atmosphere over the temperature range of 0–800 °C. The TG/DTA spectra of DPMNPH–CdI_2 complex showed two distinct steps of weight loss (Fig. 5S). The simultaneous TG curve of the complex revealed that upon heating it starts to lose the solvent ($CHCl_3$) molecules at 25 °C and continues up to 80 °C with endothermic sign of DTA at 45 °C. The observed weight loss (26.2%) is slightly lower than the calculated one (27.1%), corresponding to two $CHCl_3$ molecules of crystallization per formula unit. The crystalline sample turned into amorphous powders upon removal of the solvent molecules. The second decomposition stage starts from 380 °C and ends at 600 °C with one broad DTA exothermic signs at 402 °C corresponding to the loss of the iodide and organic moiety leaving cadmium oxide as metallic residue. This was analyzed by IR spectra and identified as (CdO, 18.2%).

Table 2
Bond lengths [Å] and angles [°] for DPMNPH–CdI_2.

Cd(1)–N(31)	2.336(4)
Cd(1)–N(11)	2.349(3)
Cd(1)–N(5)	2.368(3)
Cd(1)–I(2)	2.7197(5)
Cd(1)–I(3)	2.7656(5)
N(31)–Cd(1)–N(11)	134.40(12)
N(31)–Cd(1)–N(5)	68.26(12)
N(11)–Cd(1)–N(5)	67.63(12)
N(31)–Cd(1)–I(2)	103.57(8)
N(11)–Cd(1)–I(2)	102.12(8)
N(5)–Cd(1)–I(2)	139.28(8)
N(31)–Cd(1)–I(3)	103.29(8)
N(11)–Cd(1)–I(3)	96.15(8)
N(5)–Cd(1)–I(3)	101.51(8)
I(2)–Cd(1)–I(3)	119.015(14)

X-ray structural analyses for DPMNPH–CdI_2 complex

The molecular structure and packing view of DPMNPH–CdI_2 complex are shown in Figs. 2 and 3, respectively. Selected bond distances and angles are given in Table 2. The coordination environment of Cd(II) ion complex crystallizes in triclinic P-1 space group with two molecular complex units and two chloroform solvent molecules per unit cell. Cd(II) complex contains a tridentate DPMNPH ligand and two iodide atoms coordinated to Cd(II) ion to reveal a distorted trigonal bipyramidal geometry with two chloroform molecules of solvation in the unit cell. The coordination environment around the cadmium(II) ion is such that the ligands are assembled in a way that atoms N11, N31 and N5 occupy the axial positions with Cd-N11, Cd-N31 and Cd-N5 distances of 2.349(3), 2.336(4) and 2.368(3) Å, respectively. Interestingly, the dimensions of the intramolecular hydrogen bond N4 – H4···N21 are 0.78(6) Å, 2.07(6) Å, 2.674(5) Å, and N4 – H4 – N21 angle of 134(5)°. Same intramolecular hydrogen bonding PyN···H – N is expected in optimization structure of the free ligand (Fig. 1). The chloroform solvate molecules serve to cement the neutral molecular complexes together; alternating complex···chloroform···complex chains that run along the a-axis with I2···Cl51, I3···Cl53, I3···Cl41 contact distances of 3.621, 3.582, and 3.624 Å respectively (Fig. 4). Some chloroform chlorine makes short contacts with the centroids of pyridinic rings of the ligand generating a 3D network. Cl42···centroid of N21 C22 C23 C24 C25 C26 distance is only 3.512 Å, Cl41···centroid of N31 C32 C33 C34 C35 C36 distance is 3.972 Å (Fig. 5).

Conclusion

Cadmium(II) compounds in combination with DPMNPH ligand are synthesized and X-ray crystallographically and spectroscopically

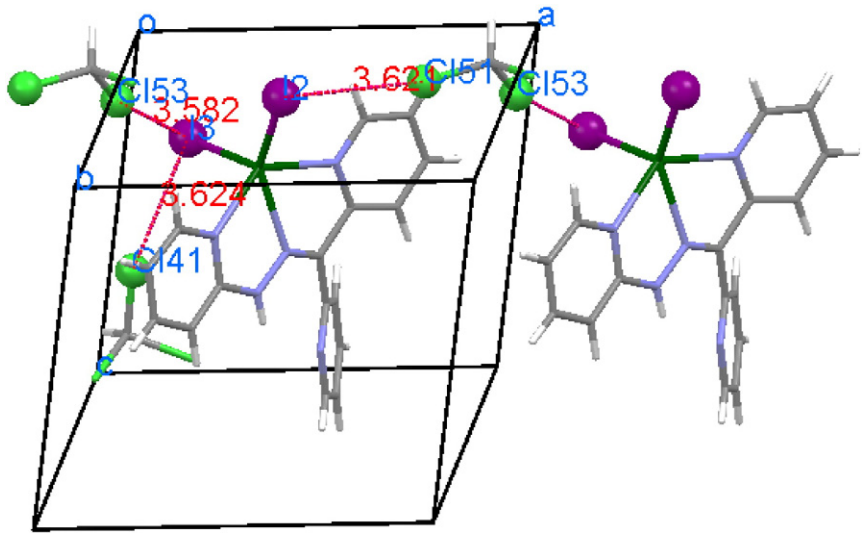


Fig. 4. I–Cl contacts generating a chain that runs along the a-axis.

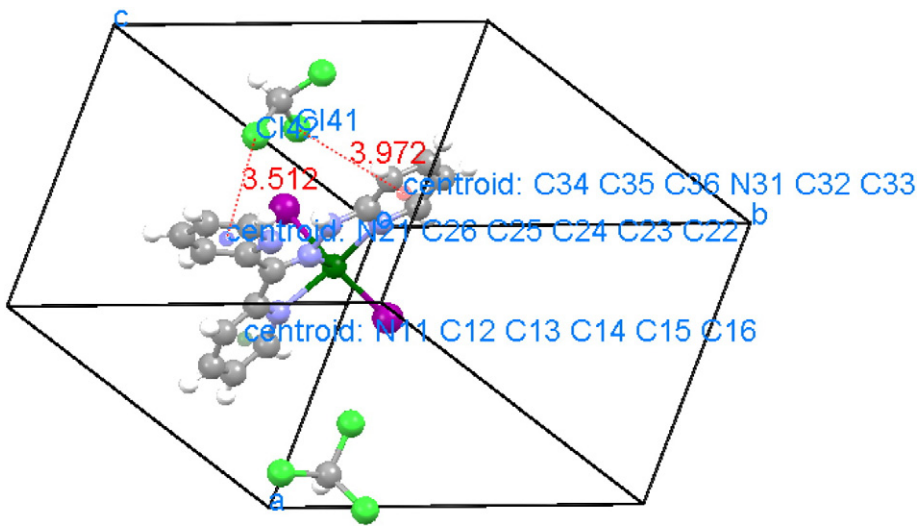


Fig. 5. Cl of solvent, chloroform, in proximity to the centroids of pyridinic rings in the complex indicating halogen–pi interactions that stabilizes the 3D network.

characterized. The ligand behaves as a neutral polydentate and serves as a neutral 3N donor, donating to Cd(II) center. The physical and spectral data suggest complexes have a distorted trigonal bipyramidal geometry. Intramolecular hydrogen bonding N – H···N – Py has also been observed. It is expected that these complexes will be a new series of three coordinated complexes of Cd(II) ions.

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Appendix A. Supplementary material

869631 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk./data_request/cif. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.inoche.2014.02.036.

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