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Synthesis, structure and properties of hexacoordinated compounds of cadmium(II) halides/pseudohalides containing a pentadentate N-donor Schiff base

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ABSTRACT

Five hexacoordinated compounds of type [Cd(L)(X)]Y·*n*MeCN (**1–5**) [L = N,N′-(bis(pyridin-2-yl)benzylidene)diethylenetriamine; Y = PF_6^-, *n* = 1; X = Cl^- (**1**), Br^- (**2**), I^- (**3**) and Y = PF_6^-, *n* = 0, X = N_3^-, (**4**); Y = ClO_4^-, *n* = 0, X = NCO^-, (**5**)] are synthesized and characterized. Structures of all the compounds are solved by X-ray diffraction measurements. Structural analyses reveal that each cadmium(II) center adopts a distorted octahedral geometry bound by five N atoms of L along with terminal halide in **1–3** and N atom of terminal pseudohalide in **4** and **5**. Intermolecular N—H···O, C—H···O, N—H···F and C—H···F hydrogen bondings and C—H···π interactions as is the case lead to different crystalline aggregates in **1–5**. The complexes display intraligand $^1(\pi-\pi^*)$ fluorescence in DMF solutions at room temperature.

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1. Introduction

Research on design and synthesis [1,2] of mono-, di- and polynuclear coordination compounds of cadmium(II) [3–8] are of great interest for the preparation of functional materials with specific electronic and optoelectronic properties [9,10]. One-pot [11,12] reactions in appropriate molar ratios of the building units held together by covalent [13] as well as non-covalent [14–17] bonds result in veritable molecular and crystalline architectures [17–20]. We are also interested in this field [21–25] to isolate different cadmium(II) compounds with interesting molecular properties using multidentate N-donor Schiff bases in combination with halides/pseudohalides. The coordination behaviors of Schiff bases [26,27] are of great interest because of their ease of preparation, structural variety, varied denticities and subtle steric and/or electronic effects leading to complexes of different dimensionalities. Halides [28–31] and pseudohalides [32–35] are suitable terminal/bridging units which in combination with organic ligands result in different mono-, di-, polynuclear coordination molecules and supramolecular entities. Recently, we examined coordination behavior of thiocyanate [21] and dicyanamide (dca) [25] towards cadmium(II) in combination with a pentadentate N-donor Schiff base, N,N′-(bis(pyridin-2-yl)benzylidene)diethylenetriamine (L, Scheme 1) and structurally characterized one heptacoordinated monomer [Cd(L)(NCS)($OClO_3$)] and two 1D coordination polymers of the type $[Cd(L)(dca)]_n(ClO_4/PF_6)_n$. This work stems from our interest to make a thorough study on cadmium(II)-L chemistry in combination with halides like chloride, bromide and iodide and pseudohalides such as azide and cyanate towards preparation of new molecular and crystalline aggregates through covalent bonds and non-covalent interactions. We have successfully isolated five hexacoordinated compounds of type [Cd(L)(X)]Y·*n*MeCN (**1–5**) [Y = PF_6^-, *n* = 1; X = Cl^- (**1**), Br^- (**2**), I^- (**3**) and Y = PF_6^-, *n* = 0, X = N_3^-, (**4**); Y = ClO_4^-, *n* = 0, X = NCO^-, (**5**)]. The details of syntheses, characterizations, X-ray structures and molecular properties of these new compounds are described below.

2. Experimental

2.1. General remarks and physical measurements

2.1.1. Materials

High purity diethylenetriamine (SRL, India), 2-benzoylpyridine (Lancaster, UK), cadmium(II) chloride/bromide/iodide (SRL, India), sodium azide (E. Merck, India), sodium cyanate (Lancaster, UK), cadmium(II) acetate (E. Merck, India) and ammonium hexafluorophosphate (Fluka, Germany) were purchased from respective concerns and used as received. Cadmium(II) perchlorate hexahydrate was prepared [36] by treatment of the corresponding cadmium(II)

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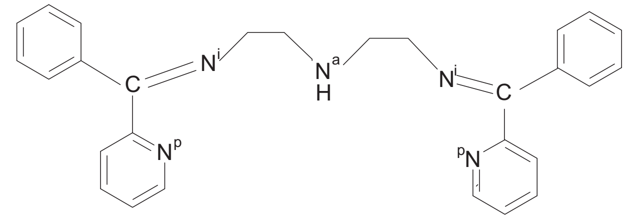

(L)

Scheme 1.

carbonate (E. Merck, India) with perchloric acid (E. Merck, India) followed by slow evaporation on a steam-bath, filtration through a fine glass-frit and preserved in a desiccator containing concentrated sulfuric acid (E. Merck, India) for subsequent uses. The Schiff base, N,N′-(bis(pyridin-2-yl)benzylidene)diethylenetriamine (L), was prepared by condensation of a 1:2 M ratio of diethylentriamine and 2-benzoylpyridine following a reported method [25]. All other chemicals and solvents used were AR grade. The synthetic reactions and work-up were done in open air.

Caution! Azide and perchlorate compounds of metal ions are potentially explosive [37] especially in the presence of organic ligands. Only a small amount of these materials should be prepared and handled with care.

2.1.2. Physical measurements

Elemental analyses (carbon, hydrogen and nitrogen) were performed on a Perkin–Elmer 2400 CHNS/O elemental analyzer. IR spectra (KBr discs, 4000–300 $\mathrm{cm^{-1}}$) were recorded using a Perkin–Elmer FTIR model RX1 spectrometer. Molar conductances were measured using a Systronics conductivity meter where the cell constant was calibrated with 0.01 M KCl solution and MeCN was used as solvent. Ground state absorptions were measured with a Jasco model V-530 UV–Vis spectrophotometer. Fluorescence measurements were done using Hitachi Fluorescence Spectroflurimeter F-4500.

2.2. General synthesis of complexes

2.2.1. [Cd(L)(X)]PF_6·MeCN [X = Cl^- (**1**), Br^- (**2**) and I^- (**3**)]

L (0.433 g, 1 mmol) in acetonitrile (10 mL) was added dropwise to a solution of $CdCl_2 \cdot H_2O$ (0.201 g, 1 mmol) in methanol (10 mL). To the resulting light yellow solution, a methanolic solution (10 mL) of NH_4PF_6 (0.163 g, 1 mmol) was added slowly with constant stirring. The final light yellow solution was filtered and left for slow evaporation in air. After a week colorless crystals of **1** that separated, were washed with hexane and dried *in vacuo* over silica gel indicator. Yield: 0.614 g (80%). For preparations and isolations of **2** and **3** in pure crystalline states, similar reaction condition and reaction stoichiometry as used in **1** were followed except that $CdBr_2 \cdot 4H_2O$ (0.344 g, 1 mmol) and CdI_2 (0.366 g, 1 mmol) instead of $CdCl_2 \cdot H_2O$ were used respectively. The light yellow solutions were processed as in **1**. Yield: **2**, 0.617 g (76%) and **3**, 0.644 g (75%). *Anal.* Calc. for $C_{30}H_{30}N_6F_6PClCd$ (**1**): C, 47.0; H, 3.9; N, 11.0. Found: C, 47.2; H, 4.1; N, 11.2%. IR (KBr, $\mathrm{cm^{-1}}$): ν(N—H) 3447, 3350, 3290; ν(C—H) 2955, 2935, 2873; ν(C═N) + ν(C═C) 1650, 1592; $\nu(PF_6)$ 843, 800, 557. Λ_M (MeCN, $\mathrm{ohm^{-1}\,cm^2\,mol^{-1}}$): 130. UV–Vis ($\lambda$, nm): 280. *Anal.* Calc. for $C_{30}H_{30}N_6F_6PBrCd$ (**2**): C, 44.4; H, 3.7; N, 10.4. Found: C, 44.5; H, 3.6; N, 10.2%. IR (KBr, $\mathrm{cm^{-1}}$): ν(N—H) 3438, 3344, 3287; ν(C—H) 2954, 2929, 2871; ν(C═N) + ν(C═C) 1649, 1591; $\nu(PF_6)$ 839, 802, 558. Λ_M (MeCN, $\mathrm{ohm^{-1}\,cm^2\,mol^{-1}}$): 125. UV–Vis ($\lambda$, nm): 281. *Anal.* Calc. for $C_{30}H_{30}N_6F_6PICd$ (**3**): C, 41.9; H, 3.5; N, 9.8. Found: C, 42.0; H, 3.4; N, 10.0%. IR (KBr, $\mathrm{cm^{-1}}$): ν(N—H) 3430, 3340, 3279; ν(C—H) 2954, 2928, 2871; ν(C═N) + ν(C═C) 1647, 1590; $\nu(PF_6)$ 842, 800, 556. Λ_M (MeCN, $\mathrm{ohm^{-1}\,cm^2\,mol^{-1}}$): 120. UV–Vis ($\lambda$, nm): 283.

2.2.2. [Cd(L)N_3]PF_6 (**4**)

To a methanolic solution (5 mL) of $Cd(OAc)_2 \cdot 2H_2O$ (0.088 g, 0.33 mmol), L (0.143 g, 0.33 mmol) in acetonitrile (10 mL) was added dropwise followed by the addition of NaN_3 (0.022 g, 0.33 mmol) and NH_4PF_6 (0.054 g, 0.33 mmol) in methanol (15 mL), that results in a light yellow solution which was processed as above in **1** to yield colorless block shaped crystals of **4**. Yield: 0.181 g (75%). *Anal.* Calc. for $C_{28}H_{27}N_8F_6PCd$ (**4**): C, 45.9; H, 3.7; N, 15.4. Found: C, 46.0; H, 3.6; N, 15.5%. IR (KBr, $\mathrm{cm^{-1}}$): ν(N—H)

Table 1
Crystallographic data and structure refinement parameters for **1–5**.

Compounds	**1**	**2**	**3**	**4**	**5**
Formula	$C_{30}H_{30}N_6F_6PClCd$	$C_{30}H_{30}N_6F_6PBrCd$	$C_{30}H_{30}N_6F_6PICd$	$C_{28}H_{27}N_8F_6PCd$	$C_{29}H_{27}N_6O_5ClCd$
Weight	767.42	811.88	858.88	732.95	687.42
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	P21/c	P21/c	P21/c	P21/n	P21/c
a (Å)	8.6090(4)	8.5438(4)	8.6908(5)	11.8900(13)	14.7391(12)
b (Å)	18.9603(8)	18.6590(8)	18.6748(10)	17.944(2)	9.0415(8)
c (Å)	19.8041(9)	19.8207(9)	19.9198(12)	14.3585(17)	21.4359(17)
β (°)	102.0670(10)	100.3040(10)	98.3350(10)	104.454(2)	100.601(2)
V (Å^3)	3161.2(2)	3108.8(2)	3198.8(3)	2966.5(6)	2807.9(4)
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
ρ_{calcd} (gm cm^{-3})	1.612	1.735	1.783	1.641	1.626
Z	4	4	4	4	4
T (K)	120(2)	120(2)	120(2)	100(2)	305(2)
μ (mm^{-1})	0.893	2.031	1.764	0.862	0.924
F (0 0 0)	1544	691	1688	1472	1392
θ ranges (°)	1.50–25.00	1.51–25.16	1.50–23.70	1.85 to 25.00	1.41–25.00
$h/k/l$	−10, 9/−22, 22/−23, 23	−10, 10/−22, 22/−23, 23	−9, 9/−21, 21/−22, 22	−16,17/−21,21/−16,17	−17, 17/−10, 10/−25, 25
Reflections collected	5581	5553	4846	5226	30,757
Independent reflections (R_{int})	4624(0.044)	4314 (0.066)	3720 (0.074)	4350 (0.074)	4952 (0.036)
Data/restraints/parameters	4624/0/407	4314/0/407	3720/0/407	4350/0/401	4952/0/379
Goodness-of-fit on F^2	1.144	1.045	1.040	1.018	1.090
Final R indices [$I > 2\sigma(I)$]	R = 0.0366, wR = 0.1045	R = 0.0352, wR = 0.0777	R = 0.0356, wR = 0.0658	R = 0.0344, wR = 0.0823	R = 0.0231, wR = 0.0578
R indices (all data)	R = 0.0462, wR = 0.1109	R = 0.0527, wR = 0.0849	R = 0.0566, wR = 0.0731	R = 0.0444, wR = 0.0880	R = 0.0209, wR = 0.0565
Largest peak and hole (eÅ^{-3})	0.817 and −0.531	0.807 and −0.588	0.0632 and −0.536	0.912 and −0.659	0.343 and −0.417

Weighting scheme: $R = \sum \| |F_o| - |F_c| | / \sum |F_o|$, $wR = \left[\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2\right]^{1/2}$, calcd $w = 1/[\sigma^2(F_o^2) + (xP)^2 + yP]$; x = 0.0609 (for **1**), 0.0375 (for **2**), 0.0209 (for **3**), 0.0386 (for **4**), 0.0311 (for **5**), and y = 3.577 (for **1**), 1.4643 (for **2**), 5.3544 (for **3**), 2.1211 (for **4**), 1.1029 (for **5**); where $P = (F_o^2 + 2F_c^2)/3$.

3430, 3353, 3295; ν(C—H) 2945, 2922, 2879; ν(N=N=N) 2035; ν(C=N) + ν(C=C) 1648, 1593; $\nu(PF_6)$ 842, 802, 557. Λ_M (MeCN, $ohm^{-1}\ cm^2\ mol^{-1}$): 110. UV–Vis (λ_{max}, nm): 280.

2.2.3. [Cd(L)(NCO)]ClO_4 (**5**)

An acetonitrilic solution (10 mL) of L (0.143 g, 0.33 mmol) was added dropwise to a solution containing a mixture of $Cd(ClO_4)_2$.6-H_2O (0.139 g, 0.33 mmol) and NaNCO (0.022 g, 0.33 mmol) in methanol (20 mL). The reaction mixture was processed as above in **1** to get pure **5**. Yield: 0.163 g (72%). *Anal.* Calc. for $C_{29}H_{27}N_6O_5ClCd$ (**5**): C, 50.7; H, 4.0; N, 12.3. Found: C, 50.8; H, 4.1; N, 12.4%. IR (KBr, cm^{-1}): ν(N—H) 3450, 3342, 3293; ν(C—H) 2950, 2935, 2882; ν(NCO) 2205; ν(C=N) + ν(C=C) 1648, 1590; $\nu(ClO_4)$ 1111, 1087, 622. Λ_M (MeCN, $ohm^{-1}\ cm^2\ mol^{-1}$): 115. UV–Vis (λ_{max}, nm): 282.

2.3. X-ray crystallographic study

Diffraction data of the single crystals of **1–5** were collected at 120(2) K (for **1**–**3**), 100(2) K (for **4**) and 305(2) K (for **5**) on a Bruker AXS SMART APEX-II CCD area-detector diffractometer using graphite monochromated Mo Kα radiation. The unit cell parameters were obtained from SAINT [38] and absorption corrections were performed with SADABS [39]. The structures were solved by direct methods and refined by full-matrix least-squares method based on F^2 using SHELXL-97 [40] for **1**, **4** and **5** and SHELXTL [40] for **2** and **3**. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were fixed geometrically and refined using a riding model. All calculations were carried out using SHELXL-97, SHELXTL, CAMERON [41], PARST [42], Mercury 2.3 [43] and ORTEP-3 [44] programs. A summary of the crystallographic data and structure determination parameters is given in Table 1.

3. Results and discussion

3.1. Synthesis and formulation

The hexacoordinated mononuclear compounds of the type [Cd(L)(Cl/Br/I)]PF_6·MeCN (**1**/**2**/**3**) were isolated as colorless crystals through one-pot synthesis of 1:1:1 M ratio of the respective cadmium(II) halide salts, pentadentate Schiff base (L) and NH_4PF_6 from methanol–acetonitrile (2:1) solution mixtures at room temperature. Use of 1:1:1:1 M ratio of $Cd(OAc)_2$·$2H_2O$, L, NaN_3 and NH_4PF_6 in the same solvent mixture results in **4**. Compound **5** was obtained in good yield through self-assembly of 1:1:1 M ratio of $Cd(ClO_4)_2$·$6H_2O$, L and NaNCO. The reactions are summarized in Eqs. (1)–(3):

$$CdX_2\cdot nH_2O + L + NH_4PF_6 \xrightarrow[298K]{MeOH-MeCN} \underset{X\ =\ Cl^-(\mathbf{1})/Br^-(\mathbf{2})/I^-(\mathbf{3})}{[Cd(L)(X)]PF_6\cdot MeCN} \quad (1)$$

$$(n = 1,\ X = Cl;\ n = 4,\ X = Br\ \text{and}\ n = 0,\ X = I)$$

$$Cd(OAc)_2\cdot 2H_2O + L + NaN_3 + NH_4PF_6 \xrightarrow[298K]{MeOH-MeCN} \underset{(\mathbf{4})}{[Cd(L)(N_3)]PF_6} \quad (2)$$

$$Cd(ClO_4)_2\cdot 6H_2O + L + NaNCO \xrightarrow[298K]{MeOH-MeCN} \underset{(\mathbf{5})}{[Cd(L)(NCO)]ClO_4} \quad (3)$$

The new complexes were characterized by microanalytical (C, H and N), spectroscopic, thermal and other physicochemical results. The microanalytical data are in good conformity with the formulations **1–5**. The moisture-insensitive complexes are stable over long periods of time in powdery and crystalline states and are soluble in methanol, ethanol, acetonitrile, dimethylformamide and dimethylsulfoxide but are insoluble in water. In MeCN solutions, **1–5** behave as 1:1 electrolytes [45] as reflected in their respective conductivity values (vide Section 2). In IR spectra, the complexes show ν(N—H) stretching frequencies of L lying within the range 3450–3270 cm^{-1}. Several weak bands in the range 2960–2870 cm^{-1} assignable to aliphatic C—H stretching vibration [46] are seen in all the compounds. ν(C=N) plus ν(C=C) stretching vibrations of the metal-bound Schiff base (L) are observed within 1650–1590 cm^{-1} range. In **4**, asymmetric azide stretch appears as a strong band at 2035 cm^{-1}. Compound **5** shows characteristic asymmetric cyanate stretching vibration at 2205 cm^{-1}; this is substantially higher than free ion value ($\sim$2155 cm^{-1}) [46,47] and is consistent [48] with N-bonding rather than O-coordination. Additionally, hexafluorophosphate stretches in **1–4** and perchlorate bands in **5** (vide Section 2) [46] exhibit splittings which is attributed to some kind of hydrogen bondings with the counter anions. X-ray study corroborates this hypothesis.

Colorless DMF solutions of compounds **1–5** show ligand-based transitions at $\sim$280 nm presumably due to n—π^*/π—π^* transition [49,50].

3.2. Description of the structures of the complexes (**1**–**5**)

Single crystal X-ray structure analyses show that compounds **1**–**5** consist of mononuclear (0D) units which are further engaged in different kinds of cooperative hydrogen bondings like N—H···F, C—H···F, N—H···O and C—H···O and C—H···π interactions as is the case among themselves resulting in different supramolecular architectures. ORTEP diagrams with atom numbering schemes and perspective views of the crystalline architectures in **1** and **4** are shown in Figs. 1–4 and for **2**, **3** and **5** in Figs. S1–S7. Selected bond distances and bond angles relevant to the metal coordination spheres and the non-covalent bonding parameters are set in Tables 2 and 3.

3.2.1. [Cd(L)(Cl)]PF_6·MeCN (**1**), [Cd(L)(Br)]PF_6·MeCN (**2**) and [Cd(L)(I)]PF_6·MeCN (**3**)

The structures (Figs. 1, S1 and S3) of **1**–**3** are made up of $[Cd(L)(X)]^+$ cation [X = Cl^-, **1**; Br^-, **2**; I^-, **3**], PF_6^- counter anion and a solvent molecule, MeCN. The overall geometry at the cadmium(II) center is best described as a distorted octahedron with a CdN_5X chromophore ligated by five N (N1, N2, N3, N4 and N5) atoms of L and one terminal halide (Cl^- for **1**, Br^- for **2** and I^- for **3**). Two N^p (N4, N5 for **1**, N1, N4 for **2** and N1, N3 for **3**), one N^i (N3 for **1** and **2** and N4 for **3**) and one N^a (N2 for **1** and N5 for **2** and **3**) atoms [N^p = N(pyridine); N^i = N(imine) and N^a = N(amine)] of L define the equatorial plane and the remaining N^i (N1 for **1**, N2 for **2** and **3**) atom of L and one terminal halide (Cl^- for **1**, Br^- for **2** and I^- for **3**) occupy the axial sites. The *cisoid* and *transoid* angles (Table 2) around the metal center are in line with strong distortion from an idealized octahedral geometry due to the asymmetric nature of the bound Schiff base. The Cd—Cl bond distance [2.4890(11) Å] in **1** is comparable with the Cd—N bond distances, but larger ionic radii of bromide and iodide in **2** and **3**, respectively result in longer Cd—X distances [2.6247(5) Å in **2** and 2.7997(5) Å in **3**] over Cd—N bond lengths (Table 2). The differences among the Cd—Cl (in **1**), Cd—Br (in **2**) and Cd—I (in **3**) (vide Table 2) bond distances correspond approximately to the differences of the ionic radii of the halides [31]. Each metal center in **1–3** has four 5-membered chelate loops with bite angles N(3)—Cd(1)—N(4) 68.35(10)°, N(1)—Cd(1)—N(5) 68.43(9)°, N(3)—Cd(1)—N(2) 70.89(10)° and N(1)—Cd(1)—N(2) 70.20(10)° for **1**; N2—Cd1—N1 68.51(11)°, N2—Cd1—N5 70.38(10)°, N3—Cd1—N5 71.10(11)° and N3—Cd1—N4 68.52(11)° for **2** and N4—Cd1—N1 68.62(15)°, N4—Cd1—N5 70.96(14)°, N2—Cd1—N5 70.80(14) ° and N2—Cd1—N3 68.62(14)° for **3**. The ethylenic arms of the Schiff base in **1–3** are to some extent puckered

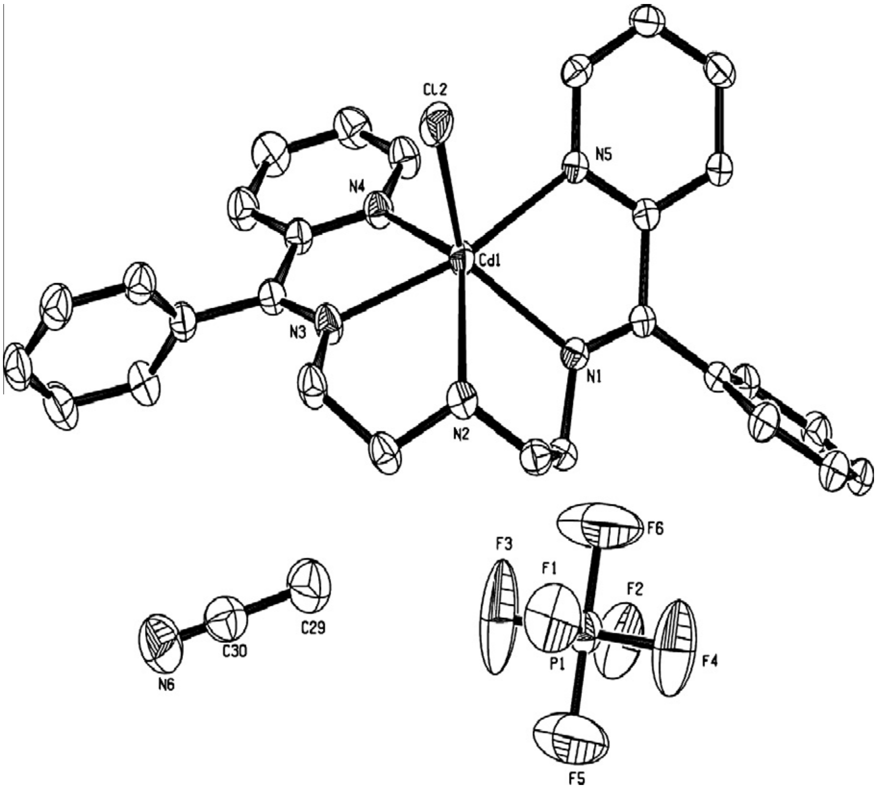

Fig. 1. An ORTEP diagram of $[Cd(L)Cl]PF_6.MeCN$ (**1**) with atom numbering scheme (30% probability ellipsoids for all non-hydrogen atoms).

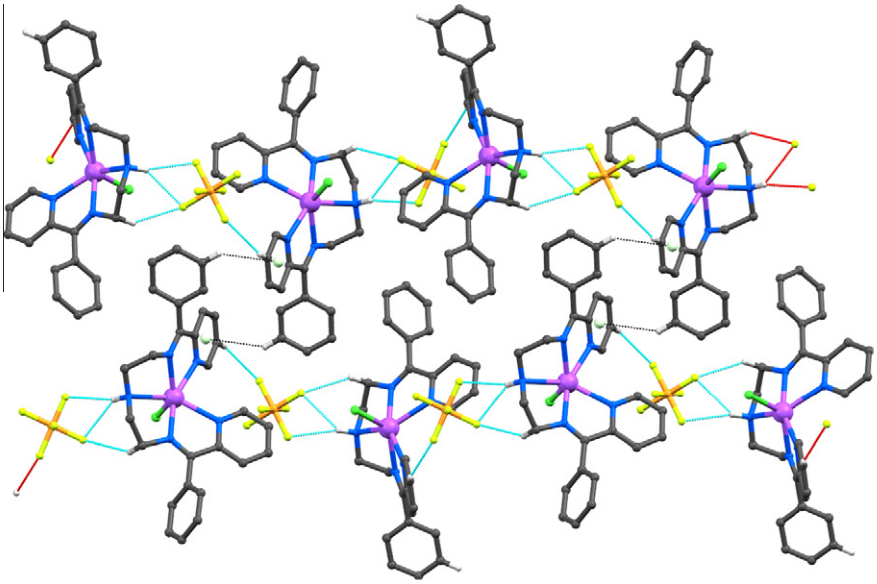

Fig. 2. A perspective view of 2D sheet structure in **1** formed by cooperative double N—H···F and C—H···F hydrogen bonds and C—H···π interaction in *bc*-plane.

due to sp^3 hybridization of the saturated fragment of the chelating L and bond angles deviate (vide Table 2) from the ideal value (109.5°). The metal(II) center in **1–3** departs 0.251 Å, 0.214 Å and 0.197 Å, respectively from the corresponding mean plane (N2, N3, N4, N5 for **1**, N1, N3, N4, N5 for **2** and **3**) towards the axial halide. Among the four equatorial nitrogens N3, N5 in **1**, N1, N3 in **2** and N3, N4 in **3** shift (N3, 0.199 Å, N5, 0.095 Å in **1**; N1, 0.086 Å and N3, 0.180 Å in **2**, and N3, 0.083 Å and N4, 0.175 Å in **3**) towards the axial halide whereas N2, N4 in **1**, N4, N5 in **2** and N1, N5 in **3** show considerable deviation (N2, 0.123 Å and N4, 0.171 Å in **1**, N4, 0.155 Å and N5, 0.112 Å in **2**, and N1, 0.150 Å and N5, 0.108 Å in **3**) towards the axial N^i atom from the mean plane.

In the crystal packing of **1**, the $[Cd(L)Cl]^+$ cations are associated by double N—H···F and C—H···F hydrogen bonds (Table 3) into 1D chain along *b*-axis. These chains are further interconnected along *c*-axis by single C—H···π interaction (Table 3) involving H (H6) atom of the ligand framework and π-cloud of one of the benzene [Cg7: C(11)—C(12)—C(26)—C(25)—C(24)—C(13)] rings into a 2D sheet structure parallel to the *bc*-plane (Fig. 2). The monomeric 0D units of **2** are packed through N—H···F and C—H···F hydrogen bonds

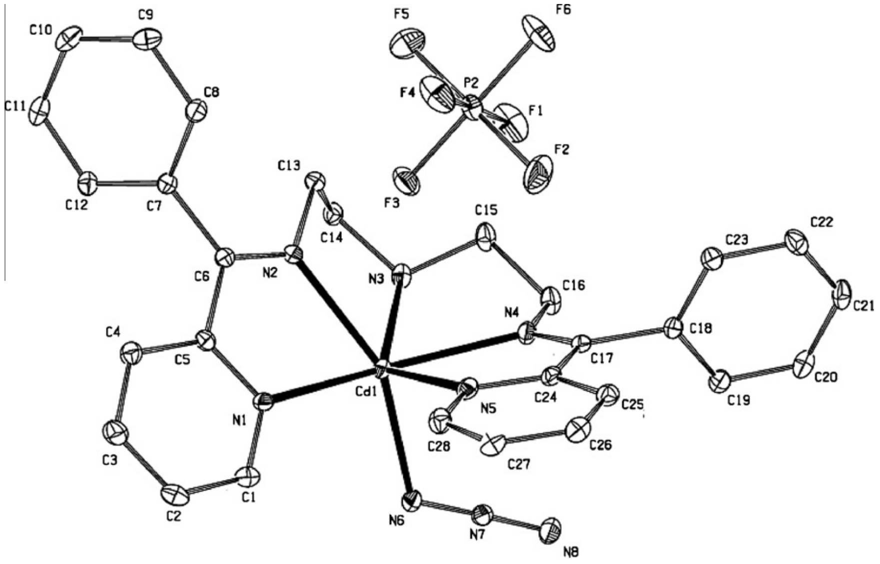

Fig. 3. An ORTEP representation of [Cd(L)(N$_3$)]PF$_6$ (**4**) with atom labeling scheme. Thermal ellipsoids are drawn at the 20% probability level.

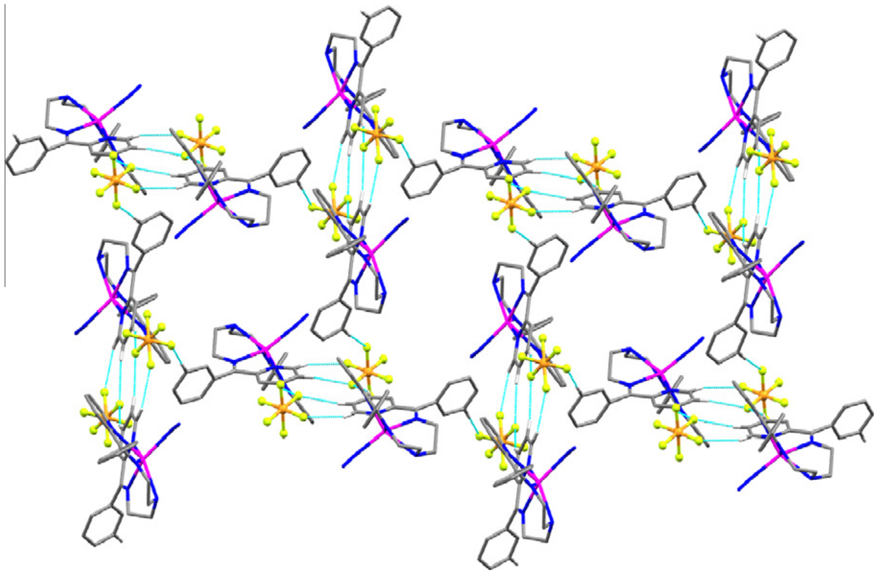

Fig. 4. 2D sheet structure in (**4**) formed by multiple C—H···F hydrogen bonds.

involving H atoms of L and F atoms of interstitial hexafluorophosphate ions coupled with single C—H···π interaction (Table 3) involving H atoms of L and π-cloud of one of the pyridine rings [Cg(5): N(1)—C(1)—C(2)—C(3)—C(4)—C(5)] leading to a 2D supramolecular architecture parallel to the *bc*-plane. This is further stabilized by another C—H···π interaction involving H (H33B) atom of the solvent molecule and π-cloud of another pyridine [Cg(6): N(4)—C(24)—C(25)—C(26)—C(27)—C(28)] ring (Fig. S2). The F atoms of the interstitial hexafluorophosphate ions and H atoms of the Schiff base and the solvent molecule in **3** are engaged in N—H···F and C—H···F hydrogen bonds interlocking the mononuclear units into a 1D chain along *b*-axis which are further connected through C—H···π interaction (Table 3) along *a*-axis resulting in a 2D sheet (Fig. S4) parallel to the *ab*-plane.

3.2.2. [Cd(L)(N$_3$)]PF$_6$ (4) and [Cd(L)(NCO)]ClO$_4$ (5)

The crystal lattices of **4** and **5** consist of mononuclear (0D) units [Cd(L)(N$_3$)]PF$_6$ and [Cd(L)(NCO)]ClO$_4$, respectively. The coordination polyhedron around each metal center in **4**/**5** (Fig. 3/Fig. S5) is best described as a distorted octahedron with a CdN$_6$ chromophore. The coordination includes the chelated pentadentate Schiff base ligated by two N^p (N1 and N5 in **4**; N3 and N6 in **5**), two N^i (N2 and N4 in **4** and **5**), one N^a (N3 for **4** and N1 for **5**) atoms of L and the sixth position is occupied by terminal azide N (N6) atom in **4** and cyanate N (N5) atom in **5**. The basal planes of **4** and **5** consist of two N^p (N1, N5 for **4** and N6, N3 for **5**), one N^i (N4 for both **4** and **5**) and one N^a (N3 for **4** and N1 for **5**) atoms of L, whereas the axial positions are occupied by the terminal pseudohalide N (N6 for **4** and N5 for **5**) and the remaining N^i (N2 for both **4** and **5**) atom of L. The equatorial Cd—N distances are in the range 2.378(3)–2.567(3) Å and 2.3417(15)–2.4603(15) Å in **4** and **5**, respectively and the axial Cd—N distances are lying between 2.264(3)–2.319(3) Å (in **4**) and 2.2010(17)–2.3196(15) Å (in **5**). The degrees of distortion from an ideal octahedral geometry are reflected in the *equatorial* [65.76(9)–133.76(8)° in **4** and 68.93(5)–130.98(5)° in **5**] and the *axial* [152.26(9)° in **4** and 141.26(6)° in **5**] bond angles. The two

Table 2
Selected bond distances (Å) and angles (°) for **1–5.**

Bond distances		Bond angles	
Compound **1**			
Cd1—N1	2.320(3)	N1—Cd1—Cl2	133.28(7)
Cd1—N3	2.337(3)	N1—Cd1—N5	68.43(9)
Cd1—N5	2.425(3)	N3—Cd1—N4	68.35(10)
Cd1—N4	2.430(3)	N5—Cd1—N4	88.72(10)
Cd1—N2	2.541(3)	N1—Cd1—N2	70.20(10)
Cd1—Cl2	2.4890(11)	N3—Cd1—N2	70.89(10)
Compound **2**			
Cd1—N2	2.314(3)	N2—Cd1—Br2	132.68(8)
Cd1—N4	2.411(3)	N2—Cd1—N1	68.51(11)
Cd1—N5	2.527(3)	N2—Cd1—N5	70.38(10)
Cd1—N3	2.339(3)	N3—Cd1—N5	71.10(11)
Cd1—N1	2.431(3)	N3—Cd1—N4	68.52(11)
Cd1—Br2	2.6247(5)	N4—Cd1—N1	89.17(10)
Compound **3**			
Cd1—N2	2.298(4)	N2—Cd1—I1	133.54(10)
Cd1—N4	2.337(4)	N2—Cd1—N3	68.62(14)
Cd1—N1	2.392(4)	N4—Cd1—N5	70.96(14)
Cd1—N3	2.448(4)	N2—Cd1—N5	70.80(14)
Cd1—N5	2.526(4)	N4—Cd1—N1	68.62(15)
I1—Cd1	2.7997(5)	N1—Cd1—N3	89.33(14)
Compound **4**			
Cd1—N1	2.415(3)	N2—Cd1—N6	152.26(9)
Cd1—N2	2.319(3)	N4—Cd1—N5	65.76(9)
Cd1—N3	2.470(3)	N4—Cd1—N3	70.70(9)
Cd1—N4	2.378(3)	N3—Cd1—N2	71.91(9)
Cd1—N5	2.567(3)	N2—Cd1—N1	68.44(8)
Cd1—N6	2.264(3)	N1—Cd1—N5	83.87(9)
N7—N8	1.160(4)	N7—N6—Cd1	117.9(2)
N7—N6	1.199(4)	N6—N7—N8	178.2(3)
Compound **5**			
Cd1—N1	2.4364(15)	N2—Cd1—N5	141.26(6)
Cd1—N2	2.3196(15)	N1—Cd1—N4	72.83(5)
Cd1—N3	2.4603(15)	N4—Cd1—N6	68.93(5)
Cd1—N4	2.3417(15)	N3—Cd1—N2	67.78(5)
Cd1—N5	2.2010(17)	N2—Cd1—N1	72.84(5)
Cd1—N6	2.4099(15)	N6—Cd1—N3	84.02(5)
N5—C6	1.162(2)	C6—N5—Cd1	164.96(15)
C6—O5	1.208(2)	N5—C6—O5	178.0(2)

Table 3
Hydrogen bond distances (Å) and angles (°) for **1–5** and C—H···π interactions (Å, °) for **1–3.**

Compound	D—H···A	D—H	H···A	D···A	D—H···A
1	N2—H2···F1^{a}	0.91	2.42	3.268(5)	155
	N2—H2···F2^{a}	0.91	2.51	3.262(5)	140
	C6—H6···F4^{b}	0.93	2.54	3.252(7)	134
	C22—H22B···F2^{a}	0.97	2.50	3.279(5)	137
2	N5—H5···F1^{c}	0.91	2.54	3.284(4)	139
	N5—H5···F4^{c}	0.91	2.33	3.175(5)	154
	C2—H2···F2^{d}	0.93	2.50	3.227(6)	135
	C30—H30A···F1^{c}	0.97	2.47	3.256(5)	139
3	N5—H5···F6^{a}	0.91	2.29	3.111(5)	150
	C13—H13B···F4^{a}	0.97	2.50	3.291(7)	138
	C27—H27···F3^{b}	0.93	2.54	3.229(7)	131
	C30—H30B···F5^{e}	0.96	2.55	3.083(10)	115
4	C1—H1···F4^{i}	0.93	2.52	3.287(4)	140
	C2—H2···F6^{i}	0.93	2.50	3.358(4)	154
	C3—H3···F6^{j}	0.93	2.36	3.254(5)	162
	C11—H11···F2^{k}	0.93	2.55	3.467(4)	171
5	N1—H1···O4^{d}	0.91	2.29	3.129(2)	152
	C9—H9·····O5^{a}	0.93	2.58	3.509(2)	174
	C10—H10···O2^{l}	0.93	2.48	3.388(3)	164
	C14—H14...O3	0.93	2.56	3.468(3)	167
	C23—H23···O4^{m}	0.93	2.50	3.334(3)	149
1	C6—H6···Cg7^{f}	0.93	3.00	3.629(4)	127
2	C9—H9···Cg5^{g}	0.93	2.84	3.627(4)	143
	C33—H33B···Cg6^{h}	0.93	2.97	3.538(6)	119
3	C27—H27···Cg8^{f}	0.93	2.90	3.555(6)	129

Symmetry codes: a = 1 – *x*, 1/2 + *y*, 3/2 – *z*; b = –1 + *x*, 1 + *y*, *z*; c = 1 – *x*, –1/2 + *y*, 1/2 – *z*; d = *x*, –1 + *y*, *z*; e = *x*, 1 + *y*, *z*; f = –1 + *x*, *y*, *z*; g = –*x*, –*y*, –*z*; h = *x*, *y*, *z*; i = 1/2 – *x*, –1/2 + *y*, 3/2 – *z*; j = –1/2 + *x*, 1/2 – *y*, –1/2 + *z*; k = 1 + *x*, *y*, *z*; l = *x*, 3/2 – *y*, 1/2 + *z*; m = 2 – *x*, –1/2 + *y*, 3/2 – *z*.

subsequent Cd—N distances: Cd1—N6 2.264(3) Å in **4** and Cd1—N5 2.2010(17) Å in **5** indicate stronger coordination through anionic cyanate in **5** over azide in **4**. The ethylenic arms of the Schiff base are to some extent puckered as is evident from the respective bond angle values (vide Table 2). The cadmium(II) centers have four five-membered chelate loops with bite angles N2—Cd1—N1 68.44(8)°, N4—Cd1—N5 65.76(9)°, N2—Cd1—N3 71.91(9)° and N4—Cd1—N3 70.70(9)° in **4** and N2—Cd1—N3 67.78(5)°, N2—Cd1—N1 72.84(5)°, N4—Cd1—N1 72.83(5)° and N4—Cd1—N6 68.93(5)° in **5**. The metal center is deviated 0.374 Å in **4** and 0.353 Å in **5** towards the axial pseudohalide N atom. The deviation of equatorial atoms in **5** (N1, 0.186 Å; N3, 0.157 Å; N4, 0.303 Å and N6, 0.274 Å) is larger than that (N1, 0.074 Å; N3, 0.096 Å; N4, 0.154 Å and N5, 0.132 Å) in **4**. The azide is more bent in **4** than the cyanate, in **5** as reflected in the respective bond angle values (vide Table 2). In **4**, the N7—N6 [1.199(4) Å] distance is larger than N7—N8 [1.160(4) Å] indicating coordination of the N6 over N8, and the length is larger than the reported [51] ones. The N5—C6 [1.162(2) Å] distance is larger and C6—O5 [1.208(2) Å] length is smaller than the expected one [52] which is in consonance with the N-coordination of terminal cyanate in **5**. The bond angle values N6—N7—N8 178.2(3)° in **4** and N5—C6—O5 178.0(2)° in **5** indicate the quasi-linearity of the terminal pseudohalides.

In the crystalline state, 0D mononuclear units of **4** are associated by multiple C—H···F hydrogen bonds (Table 3) involving H atoms of the ligand framework and F atoms of the hexafluorophosphate ions embedded among these mononuclear units resulting in a 2D sheet structure (Fig. 4). Mononuclear units of **5** pack through three kinds of C—H···O hydrogen bonds involving H atoms of the ligand backbone and O atoms of the perchlorate counter ions (Table 3) into a 2D sheet structure (Fig. S6) parallel to the *ab*-plane. These sheets are further involved in N—H···O and C—H···O hydrogen bonds along *c*-axis resulting in a 3D network structure (Fig. S7).

3.3. Luminescence behaviors

In DMF solutions, the compounds, **1–5**, show band maxima centered at ~280 nm (see Section 2). Upon photo excitations at the corresponding absorption bands in DMF solutions at 298 K compounds **1–3** show weak emission bands centered at ~400 nm whereas complexes **4** and **5** exhibit intense emission bands at

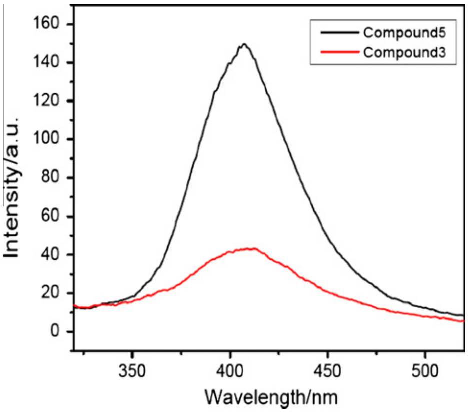

Fig. 5. Emission spectra of complexes **3** and **5** in DMF solution at 298 K.

$\sim$410 nm which are assigned to the intraligand $^1(\pi—\pi^*)$ fluorescence [25,53–55]. The halide complexes **1–3** show weak emission bands compared to the pesudohalide compounds **4** and **5** presumably due to better quenching ability of the halogens [56]. Representative emission spectra of a halide (**3**) and a pseudohalide (**5**) compounds are shown in Fig. 5.

4. Conclusion

A series of luminous cadmium(II) halide/pseudohalide complexes in combination with a pentadentate N-donor Schiff base has been synthesized and X-ray crystallographically characterized; interestingly, halide compounds with solvent of crystallization stabilizes the crystalline architectures as compared over pseudohalide ones.

Supplementary data

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic data center Nos. 767045 (**1**), 764795 (**2**), 764796 (**3**), 764797 (**4**) and 764798 (**5**). Copies of this information can be obtained, free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2011.03.039.

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