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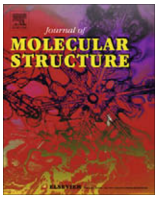

Synthesis, structure and luminescence behaviour of heptacoordinated one-dimensional coordination polymers of the type $[Cd(L)(dca)]_n(X)_n$ (L = a pentadentate Schiff base; dca = dicyanamide; X = ClO_4^-, PF_6^-)

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ABSTRACT

Two heptacoordinated one-dimensional coordination polymers of the type $[Cd(L)(dca)]_n(X)_n$ (**1** and **2**) [L = *N*,*N*′-(bis-(pyridin-2-yl)benzylidene)diethylenetriamine; dca = dicyanamide; X = ClO_4^- (**1**), PF_6^- (**2**)] have been prepared and characterized on the basis of microanalytical, spectroscopic and other physicochemical properties. Structures of **1** and **2** are solved by single crystal X-ray diffraction measurements. Structural study reveals that in both compounds each cadmium(II) center adopts a distorted pentagonal bipyramidal geometry with a CdN_7 chromophore coordinated by five N atoms of the pentadentate Schiff base and two nitrile N atoms of single bridged dca in $\mu_{1,5}$ fashion. The polynuclear units in **1** are engaged in weak N–H. . .O and C–H. . .O hydrogen bondings with perchlorate ions embedded among the chains to give a 2D sheet structure. In the long-range form, the 1D polymeric chains of **2** pack through N–H. . .F and C–H. . .F hydrogen bonds with hexafluorophosphate placed in between chains resulting a 2D continuum. The complexes display intraligand $^1(\pi-\pi^*)$ fluorescence in DMF solutions at room temperature.

1. Introduction

Polynuclear Group 12 metal ion complexes have witnessed a great interest in search of functional materials [1–5] specially with electronic [3] and optoelectronic [4] properties. The essential prerequisites for such research are the judicious choice [6] of organic spacers and inorganic/organic bridges that may lead to directed properties. Self-assembly [7] of the building units is an efficient approach towards preparation of such materials. Exploiting the variety of coordination geometries around these metal ions, diverse molecular and crystalline architectures [8,9] of different shapes and sizes [10] may be accessed through strong metal–ligand covalent bonds and multiple non-covalent bonds like hydrogen bonding [11,12] π. . .π [13], C–H. . .π [14,15] etc. interactions. Recently, we are active [16–18] to prepare different mono-, di- and polynuclear complexes of cadmium(II) in combination with multiple N-donor Schiff bases [19] and related ligands, and pseudohalides [20–22] like azide and thiocyanate towards preparation of luminous materials. To extend this work with other larger pseudohalide like dicyanamide (dca) [23,24] which is recently being studied by the coordination chemists round the world, we have examined its coordination behaviour towards cadmium(II) in combination with a neutral N-donor Schiff base, *N*,*N*′-(bis-(pyridin-2-yl)benzylidene)diethylenetriamine (L). Successfully, two heptacoordinated one-dimensional coordination polymers of the type $[Cd(L)(dca)]_n(X)_n$ (**1** and **2**) [dca = dicyanamide; X = ClO_4^- (**1**), PF_6^- (**2**)] have been prepared through reaction of a 1:1:1 M ratio of cadmium(II) salt, L and dca in MeOH at room temperature using appropriate counter anions. Structures of **1** and **2** are solved by single crystal X-ray diffraction measurements. In this paper we report the synthesis, structures, characterization and luminescence behaviour of these new complexes.

2. Experimental

2.1. General remarks and physical measurements

2.1.1. Materials

High purity 2-benzoylpyridine (Lancaster, UK), dicyanamide (Lancaster, UK), potassium hexaflurophosphate (Fluka, Germany), diethylenetriamine (SRL, India) and cadmium(II) acetate (SRL, India) were purchased from respective concerns and used as received. Cadmium(II) perchlorate hexahydrate was prepared [25] on treatment of cadmium(II) carbonate (E. Merck, India) with perchloric acid (E. Merck, India) followed by slow evaporation on

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steam-bath, filtration through fine glass-frit, and was preserved in a desiccator containing concentrated sulphuric acid (E. Merck, India) for subsequent use. All other chemicals and solvents were AR grade and were used as received.

Caution! Perchlorate compounds of metal ions are potentially explosive [26] especially in presence of organic ligands. Only small amount of the material 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 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 dry MeOH and DMF were used as solvents. Ground state absorption was measured with a Jasco model V-530 UV–vis spectrophotometer. Fluorescence measurements were done using Hitachi Fluorescence Spectroflurimeter F-4500. Time-resolved fluorescence measurements were carried out using a time-correlated single photon counting (TCSPC) spectrometer Edinburgh Instruments, model 199; a hydrogen filled coaxial flash lamp with a pulse width of 1.2 ns at FWHM and a Philips XP-2020Q photomultiplier tube were used as the excitation source and the fluorescence detector.

2.2. Synthesis of the Schiff base

2.2.1. N,N′-(bis-(pyridin-2-yl)benzylidene)diethylenetriamine (L)

2-Benzoylpyridine (0.366 g, 2 mmol) was refluxed (10 h) with diethylenetriamine (0.103 g, 1 mmol) in dehydrated alcohol. The solution was evaporated under reduced pressure to yield a yellow gummy mass that was dried and stored *in vacuo* over $CaCl_2$ for subsequent use. Yield: 0.368 g (85%). *Anal.* Calc. for $C_{28}H_{27}N_5$ (L): C, 77.5; H, 6.3; N, 16.2; Found: C, 77.4; H, 6.2; N, 16.4%; IR (KBr, cm^{-1}): ν(C=N) 1624, 1595. UV–vis (λ, nm): 368, 273.

2.3. General synthesis of the complexes

2.3.1. $[Cd(L)(dca)]_n(ClO_4)_n$ (**1**)

$Cd(ClO_4)_2\cdot 6H_2O$ (0.419 g, 1 mmol) and L (0.433 g, 1 mmol) were taken in methanol (each with 5 mL) and mixed together slowly. To the resulting light yellow solution, a methanolic solution (5 mL) of sodium dicyanamide (0.089 g, 1 mmol) was added dropwise. The light yellow solution was left undisturbed in air for slow evaporation. After a few days colourless single crystals of **1** that separated, were washed with water and dried *in vacuo* over silica gel indicator. Yield: 0.569 g (80%). *Anal.* Calc. for $C_{30}H_{27}N_8O_4ClCd$ (**1**): C, 50.6; H, 3.8; N, 15.8. Found: C, 50.4; H, 3.6; N, 15.6%. IR (KBr, cm^{-1}): ν(NH) 3328, 3279; ν(CH) 2965, 2878; $\nu_{as}+\nu_s$(C≡N) 2272; ν_{as}(C≡N) 2226; ν_s(C≡N) 2141; ν(C=N) 1620, 1592; ν_{as}(C–N) 1322; ν_s(C–N) 927; $\nu(ClO_4)$ 1104, 623. UV–vis (λ, nm): 281.

2.3.2. $[Cd(L)(dca)]_n(PF_6)_n$ (**2**)

2.3.2.1. Method A. A methanolic solution (5 mL) of L (0.433 g, 1 mmol) was added slowly to a solution (5 mL) of $Cd(OAc)_2\cdot 2H_2O$ (0.267 g, 1 mmol) in the same solvent. Sodium dicyanamide (0.089 g, 1 mmol) in methanol (5 mL) followed by KPF_6 (0.368 g, 2 mmol) solution (5 mL) in the same solvent were added to this solution mixture. The resulting light yellow solution was filtered and left undisturbed in an air for slow evaporation. On the next day colourless crystals of **2** were produced that were collected in pure form as described in **1.** Yield: 0.644 (85%).

2.3.2.2. Method B. Complex **2** was prepared by metathesis of **1** with KPF_6 in 1:2 M ratio from an methanolic solution with constant stirring for 45 min at room temperature. The resulting light yellow solution was filtered and left in air for slow evaporation. Colourless shining microcrystals of **2** were obtained in almost quantitative yield.

The microanalytical and spectroscopic results of **2** obtained from both the methods (A and B) are similar. *Anal.* Calc. for $C_{30}H_{27}N_8F_6PCd$ (**2**): C, 47.6; H, 3.6; N, 14.9. Found: C, 47.4; H, 3.4; N, 14.9%. IR (KBr, cm^{-1}): ν(NH) 3315, 3269; ν(CH) 2948, 2868; $\nu_{as}+\nu_s$(C≡N) 2275; ν_{as}(C≡N) 2220; ν_s(C≡N) 2148; ν(C=N) 1618, 1593; ν_{as}(C–N) 1318; ν_s(C–N) 954; $\nu(PF_6)$ 846, 542. UV–vis (λ, nm): 281.

2.4. X-ray crystallographic study

Single crystals of **1** and **2** suitable for X-ray analyses were selected from those obtained by slow evaporation of methanolic solutions of the reaction mixtures at 298 K. Diffraction data were collected at 296 K 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; absorption corrections were performed with SADABS [27]. A summary of the crystallographic data and structure determination parameters are given in Table 1. The unique reflections were recorded using the ω scan technique and structures were solved by direct methods using SHELX-97 [28]. All hydrogen atoms were fixed geometrically and refined using a riding model and the calculations were carried out using PLATON [29] and ORTEP-32 [30].

3. Results and discussion

3.1. Synthesis and formulation

The ligand (L, Scheme 1) was synthesized by refluxing a 1:2 M ratio of diethylenetriamine and 2-benzoylpyridine in boiling alcohol. Colourless powders of heptacoordinated one-dimensional coordination polymers of the type $[Cd(L)(dca)]_n(X)_n$ (**1** and **2**) [X = ClO_4^- (**1**), PF_6^- (**2**)] were obtained in good yields through reaction of a 1:1:1 M ratio of metal (II) perchlorate or acetate, Schiff base ligand and pseudohalide molecular ion rod, dicyanamide. For preparation of **2,** two equivalents of potassium hexaflurophosphate was added to the reaction mixture containing 1:1:1 M ratio of cadmium(II) acetate, L and dca; **2** was also isolated by metathesis of **1** in methanol using potassium hexaflurophosphate. The reactions are summarized in Eqs. (1)–(3):

$$Cd(ClO_4)_2\cdot 6H_2O + L + dca \xrightarrow[298\ K]{MeOH} \underset{(\mathbf{1})}{[Cd(L)(dca)]_n}(ClO_4)_n \tag{1}$$

$$Cd(OAc)_2\cdot 2H_2O + L + dca \xrightarrow[KPF_6]{MeOH} \underset{(\mathbf{2})}{[Cd(L)(dca)]_n}(PF_6)_n \tag{2}$$

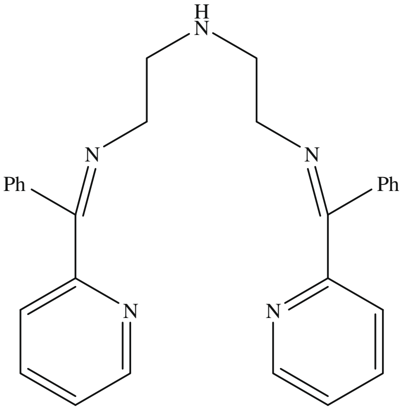
$$\underset{(\mathbf{1})}{[Cd(L)(dca)]_n}(ClO_4)_n \xrightarrow[KPF_6]{MeOH} \underset{(\mathbf{2})}{[Cd(L)(dca)]_n}(PF_6)_n \tag{3}$$

The new complexes were characterized by elemental analyses, spectroscopic studies and other physicochemical results. Microanalytical data are consistent with the formulations 1 and 2. The moisture-insensitive complexes are stable over long period of time in powdery or crystalline states and are soluble in a wide range of common organic solvents such as methanol, ethanol, acetonitrile, dimethyformamide and dimethylsulphoxide but are insoluble in water. Conductance measurements in MeOH and DMF solutions show low conductivity values (Λ_M for 1, ~50 and for 2, ~40 ohm^{-1} cm^2 mol^{-1}) reflecting [31] association of the counter ions with the metalated cationic organic frameworks in solid state as well as in solution. In IR spectra, three bands at 2272, 2226 and 2141 cm^{-1} for 1 and at 2275, 2220 and 2148 cm^{-1} for 2 are indicative of $\mu_{1,5}$-dicyanamide bridging [32,33]. The results are confirmed by X-ray structure determinations. Bands in the range 1620–1590 cm^{-1}

Table 1
Crystallographic data for **1** and **2**.

Complex	**1**	**2**
Formula	$C_{30}H_{27}N_8O_4ClCd$	$C_{30}H_{27}N_8F_6PCd$
Formula weight	711.45	756.97
Crystal system	Monoclinic	Monoclinic
Space group	Cc	Cc
a (Å)	10.7523(3)	10.8987(11)
b (Å)	22.9551(7)	23.385(3)
c (Å)	12.2789(3)	12.4357(12)
β (°)	93.4070(10)	91.741(2)
V (Å^3)	3025.32(15)	3168.0(6)
λ (Å)	0.71073	0.71073
ρ_{calcd} (gm cm^{-3})	1.562	1.587
Z	4	4
T (K)	296(2)	296(2)
μ (mm^{-1})	0.860	0.810
F (0 0 0)	1440	1520
Crystal size	0.22 × 0.17 × 0.13	0.30 × 0.21 × 0.12
θ ranges (°)	1.77 to 32.90	1.74 and 21.69
$h/k/l$	−16,16/−34,31/−18,18	−11,11/−24,24/−12,12
Reflections collected	29,693	10,971
Independent reflections	9938	3715
Data/restraints/parameters	9938/2/397	3715/418/415
Goodness-of-fit on F^2	1.021	1.050
Final R indices [$I > 2\sigma(I)$]	R = 0.0352 and wR = 0.0746	R = 0.0375 and wR = 0.0765
R indices (all data)	R = 0.0489 and wR = 0.0807	R = 0.0435 and wR = 0.0798
Largest peak and hole (eÅ^{-3})	0.608 and −0.458	0.585 and −0.381

Weighting scheme: $R = \sum|F_o| - |F_c||/\sum|F_o|$, $wR^2 = \left[\sum w\left(F_o^2 - F_c^2\right)_2 \Big/ \sum w\left(F_o^2\right)^2\right]^{1/2}$, Calc. $w = 1\Big/\left[\sigma^2\left(F_o^2\right) + (0.0412P)^2 + 0.3828P\right]$ **1** and $w = 1\Big/\left[\sigma^2\left(F_o^2\right) + (0.0260P)^2 + 5.1125P\right]$. **2**, where $P = \left(F_o^2 + 2F_c^2\right)\Big/3$.



Scheme 1.

assignable to ν(C=N) + ν(C=C) stretching vibration of the Schiff base are routinely observed. The stretches [34] corresponding to the ν(ClO_4) at 1104 and 623 cm^{-1} in 1 and ν(PF_6) at 846 and 542 cm^{-1} in 2 are also seen as expected. Reflectance spectra (281 nm for 1 and 282 nm for 2) in Nujol and electronic spectra in DMF solutions are akin reflecting similar gross geometric and electronic structure in solid state and in solution. The transition is assignable to ligand-based charge transfer [35] as expected for d^{10} cadmium(II) complexes containing organic ligand with unsaturation on its framework.

3.2. Descriptions of the structures of $[Cd(L)(dca)]_n(ClO_4)_n$ (**1**) and $[Cd(L)(dca)]_n(PF_6)_n$ (**2**)

The structural analyses show that **1** and **2** are isomorphous and consist of 1D covalent chains running along the [1 0 1] direction. Cooperative intermolecular N–H...O and C–H...O in **1** and N–

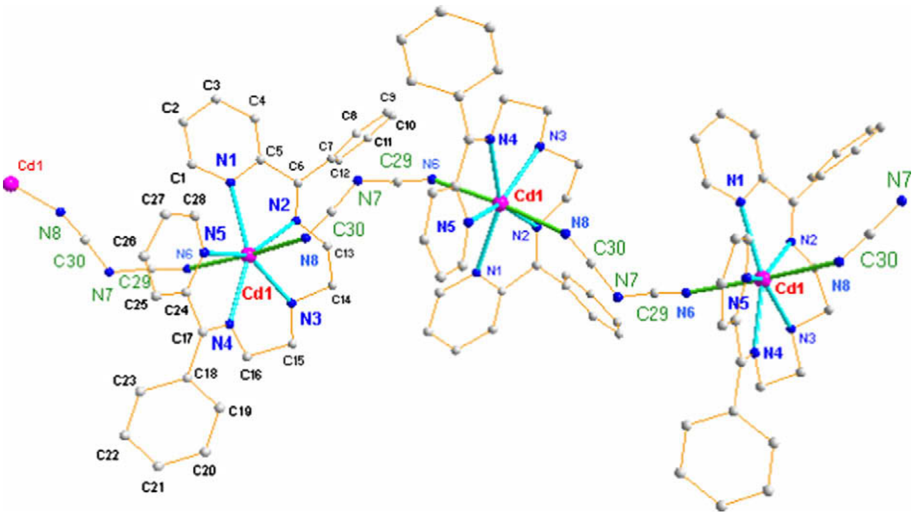


Fig. 1. An ORTEP diagram of $[Cd(L)(dca)]_n^{n+}$ with atom labeling scheme and 20% probability ellipsoids for all non-hydrogen atoms.

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

Bond distances (Å)	
Cd1–N4	2.369(2)
Cd1–N6	2.372(3)
Cd1–N8	2.380(3)
Cd1–N3	2.381(2)
Cd1–N1	2.408(2)
Cd1–N2	2.426(2)
Cd1–N5	2.470(2)
N6–C29	1.159(4)
N7–C30	1.287(5)
N7–C29	1.312(4)
N8–C30^{a}	1.169(4)
C30–N8^{b}	1.169(4)
Bond angles (°)	
N6–Cd1–N8	171.36(10)
N4–Cd1–N3	72.57(9)
N4–Cd1–N1	149.62(9)
N3–Cd1–N1	135.33(8)
N4–Cd1–N2	142.03(8)
N3–Cd1–N2	69.51(8)
N1–Cd1–N2	67.47(8)
N4–Cd1–N5	67.04(8)
N3–Cd1–N5	136.86(9)
N1–Cd1–N5	87.62(8)
N2–Cd1–N5	147.68(9)
C29–N6–Cd1	127.7(3)
C30–N7–C29	116.1(3)
N6–C29–N7	174.4(4)
C30^{a}–N8–Cd1	145.3(3)
N8^{b}–C30–N7	174.6(3)

Symmetry code: a = −1/2 + *x*, 3/2 − *y*, −1/2 + *z*; b = 1/2 + *x*, 3/2 − *y*, 1/2 + *z*.

Table 3
Selected bond distances (Å) and bond angles (°) for **2.**

Bond distances (Å)	
Cd1–N4	2.361(6)
Cd1–N8	2.373(6)
Cd1–N6	2.382(6)
Cd1–N3	2.391(6)
Cd1–N1	2.412(5)
Cd1–N2	2.439(6)
Cd1–N5	2.494(6)
N7–C29	1.306(10)
N7–C30^{a}	1.318(9)
C29–N6	1.137(8)
N8–C30	1.139(9)
C30–N7^{b}	1.318(9)
Bond angles (°)	
N8–Cd1–N6	168.6(2)
N4–Cd1–N3	71.7(2)
N4–Cd1–N1	151.3(2)
N3–Cd1–N1	134.90(19)
N4–Cd1–N2	140.1(2)
N3–Cd1–N2	68.4(2)
N1–Cd1–N2	67.64(18)
N4–Cd1–N5	66.9(2)
N3–Cd1–N5	135.91(19)
N1–Cd1–N5	88.92(18)
N2–Cd1–N5	150.0(2)
C29–N7–C30^{a}	120.0(6)
N6–C29–N7	175.0(8)
C29–N6–Cd1	150.5(6)
C30–N8–Cd1	134.2(6)
N8–C30–N7^{b}	175.1(8)

Symmetry code: a = 1/2 + *x*, 3/2 − *y*, 1/2 + *z*; b = −1/2 + *x*, 3/2 − *y*, −1/2 + *z*.

Table 4
Hydrogen bond distances (Å) and angles (°) for **1**.

D–H. . .A	D–H	H. . .A	D. . .A	D–H. . .A
N3–H3A. . .O3^{i}	0.91	2.09	2.980(5)	165
C2–H2. . .O2^{ii}	0.93	2.51	3.150(7)	127

Symmetry code: i = −1/2 + *x*, 3/2 − *y*, ½ + *z*; ii = *x*, 1 − *y*, 1/2 + *z*.

Table 5
Hydrogen bond distances (Å) and angles (°) for **2**.

D–H. . .A	D–H	H. . .A	D. . .A	D–H. . .A
N3–H3A. . .F4^{i}	0.91	2.04	2.947(8)	176
C3–H3. . .F1^{ii}	0.93	2.44	3.041(8)	123
C9–H9. . .F3^{iii}	0.93	2.46	3.249(12)	143
C27–H27. . .F4^{iv}	0.93	2.44	3.165(9)	135

Symmetry code: i = 1 + *x*, *y*, *z*; ii = 1/2 + *x*, −1/2 + *y*, *z*; iii = 3/2 + *x*, 3/2 − *y*, 1/2 + *z*; iv = 1/2 + *x*, 3/2 − *y*, 1/2 + *z*.

H. . .F and C–H. . .F in **2** hydrogen bondings link these covalent chains into 2D supramolecular sheet structures parallel to the *bc* plane. ORTEP diagram with atom numbering scheme of a typical 1D polymer viz. **1** is shown in Fig. 1. Selected bond distances and bond angles relevant to the metal coordination spheres of **1** and **2** are given in Tables 2 and 3, respectively. The hydrogen bonding parameters are set in Tables 4 and 5. Each cadmium(II) center has a distorted pentagonal bipyramidal geometry (pbp) with a CdN$_7$ chromophore. Two pyridine nitrogens (N1 and N5), two imine nitrogens (N2 and N4), one amine nitrogen (N3) of L occupy the equatorial plane; two nitrile nitrogens (N6 and N8) of two different $\mu_{1,5}$-bridged dca complete the heptacoordination and connect other neighboring cadmium(II) centers in a non-ending fashion producing the 1D chain. Distortion from the ideal geometry is due to the asymmetric nature of the bound Schiff base and the deviations of the refine angles formed at the metal center. The degrees of distortion from ideal pbp geometry are also reflected in the *equatorial* [67.04(8)–87.62(8)° in **1** and 66.9(2)–88.92(18)° in **2**] and *axial* [171.36(10)° in **1** and 168.6(2)° in **2**] bond angles. The cadmium(II) center deviates 0.056 Å from the mean plane towards N6 in both **1** and **2**. Among the five equatorial nitrogens, N1 and N4 in **1** and N2 and N5 in **2** deviate (N1, 0.355 Å and N4, 0.259 Å; N2, 0.231 Å and N5 0.334 Å) towards N8 whereas N2 and N5 in **1** and N1 and N4 in **2** show considerable deviation (N2, 0.260 Å and N5, 0.353 Å; N1, 0.322 Å and N4, 0.268 Å) towards N6 from the mean plane. The remaining nitrogen (N3) is almost on the mean plane compared to other atoms with maximum deviations 0.001 Å in **1** and 0.020 Å in **2**. The intrachain Cd. . .Cd separation in **1** (8.157 Å) is shorter than that in **2**(8.368 Å). Dicyanamide coordinates to the metal centers via $\mu_{1,5}$ bridge in a bending fashion as reflected in the bond angles C29–N6–Cd1 [127.7(3)° in **1** and 150.5(6)° in **2**] and C30–N8–Cd1 [145.3(3)° in **1** and 134.2(6)° in **2**]. The skeletal bond angles of dca are N6–C29–N7 [174.4(4)° in **1** and 175.0(8)° in

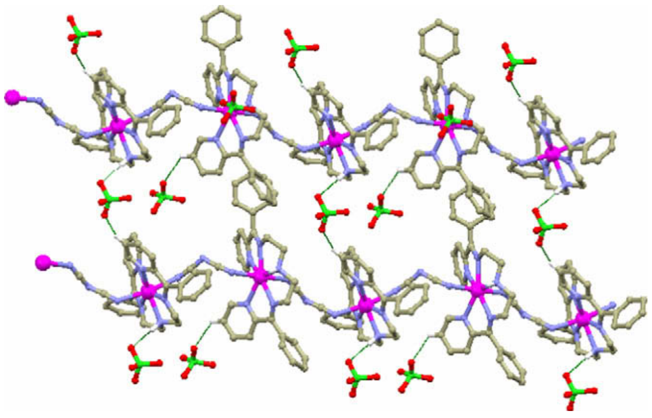


Fig. 2. Packing diagram of 2D sheet structure in **1** containing cooperative N–H. . .O and C–H. . .O hydrogen bondings along *bc*-plane.

2], C30–N7–C29 [116.1(3)° in **1** and 120.0(6)° in **2**] and N8–C30–N7 [174.6(3)° in **1** and 175.1(8)° in **2**] that reflects non-linearity of the larger pseudohalide rod.

In the crystal packing of **1,** 1D polymeric chains running along the direction [1 0 1] are engaged in single N–H. . .O and single C–H...O hydrogen bondings with the perchlorate ions embedded among the chains leading to a 2D sheet parallel to the *bc* plane (Fig. 2) with interchian Cd...Cd separation 12.674 Å. Similarly, 1D polymeric chains of **2** running in the direction [1 0 1] pack through involvement of single N–H...F and weak multiple C–H. . .F hydrogen bondings with the hexafluorophosphate ions located between the polymeric chains resulting once again in a 2D sheet parallel to the *bc* plane (Fig. 3) but with greater (12.900 Å) interchain Cd...Cd separation as compared to **1.**

3.3. Absorption and luminescence properties

In DMF solution, the Schiff base L shows absorption bands at 368 and 273 nm assignable to $n–\pi^*$ of transition of the aromatic rings. Excitation at 368 or 273 nm, L does not show any emission band. The absorption spectra of the complexes **1** and **2** show band maxima at 281 nm. Although dicyanamide, free Schiff base (L) and common cadmium(II) salts used as building units are not luminescent, interestingly the cadmium(II) complexes with this pentadentate Schiff base containing the pyridine moiety show intense fluorescence band at 570 nm (for **1**) and at 566 nm (for **2**) upon excitation at the corresponding absorption band of the complexes in DMF solutions at room temperature. The lifetimes are in the range 2.65–2.70 ns. The appearance of the fluorescence [36] upon complex formation could be inferred to the change in MO structure in the complexes compared to that in the free L. The HOMO–LUMO $n–\pi^*$ type of forbidden transition of the free L changes to $\pi–\pi^*$ type of HOMO–LUMO transition in the metal complexes. Therefore upon complexation the non-fluorescent free ligand favours fluorescence characteristic of the simple coordinated aromatic chromophore. Spectral results are set in Table 6 and a representative spectral pattern is shown in Fig. 4.

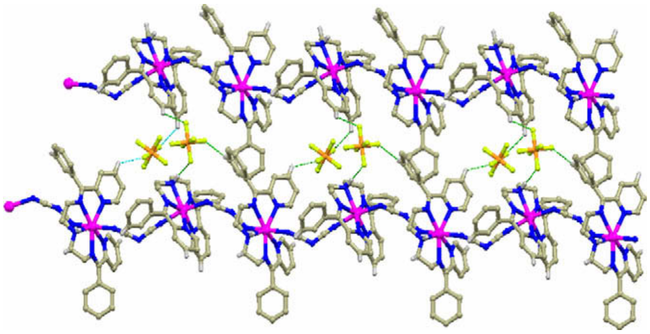


Fig. 3. Packing diagram of 2D sheet structure in **2** formed by cooperative N–H. . .F and C–H. . .F hydrogen bondings along *bc*-plane.

Table 6
Photophysical data.

Sample	Absorption (λ/nm)	Emission (λ/nm) Fluorescence[a]	Lifetime (ns)
1	281	570	2.66
2	281	566	2.68

[a] In DMF at room temperature (298 K).

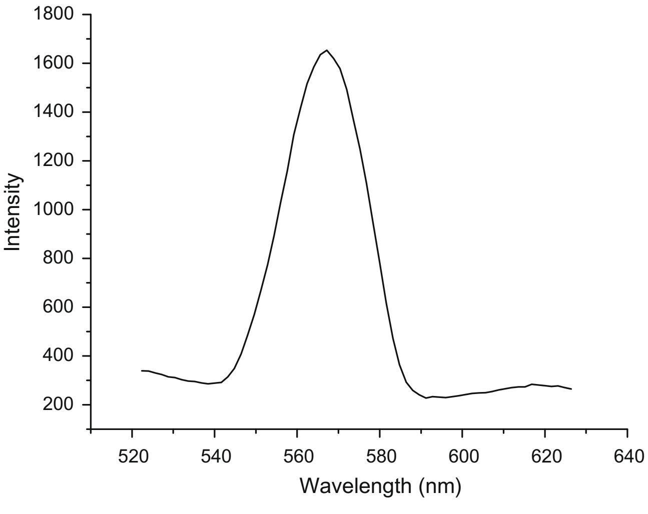


Fig. 4. Emission spectrum of **1**: fluorescence in DMF solution at 298 K (–).

4. Conclusion

Successfully we have prepared two new luminous 1D coordination polymers of cadmium(II) in combination with a Schiff base ligand and dicyanamide bridge through a single-pot reaction of the molecular building components in preassigned ratios. The interesting feature is the enhanced coordination of the 4d metal ion. The use of pentadentate ligand and larger-sized bridging unit ensures such a conformation in the coordination frames that different kinds of hydrogen bonds result in and lead to different crystalline architectures. Structures of **1** and **2** represent the reliability of combination of strong covalent bonds and weak non-covalent interactions in crystal engineering for rational designing of functional materials at molecular level.

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Appendix A. Supplementary data

Crystallographic data for the structural analyses (excluding structure factors) have been deposited with the Cambridge Crystallographic data center (CCDC Nos. 742990 for **1** and 742991 for **2**). Copies of this information can be had 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). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2009.09.043.

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