Journal of Molecular Structure 1092 (2015) 34-43

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc

Dicynamide bridged two new zig-zag 1-D Zn(II) coordination polymers of pyrimidine derived Schiff base ligands: Synthesis, crystal structures and fluorescence studies

Saugata Konar*

Department of Chemistry, Jadavpur University, Kolkata 700032, India

HIGHLIGHTS

- 2D polymeric dicynamide bridged Zn(II) complexes have been synthesized.
- X-ray crystallographic structures of Zn(II) complexes have been performed.
- Weak forces lead to various supramolecular architectures.
- The fluorescence study has been performed.

A R T I C L E I N F O

Article history: Received 25 November 2014 Received in revised form 13 February 2015 Accepted 13 February 2015 Available online 26 February 2015

Keywords: Coordination polymers Zinc (II) Dicyanamide Emission properties Supramolecular interaction

G R A P H I C A L A B S T R A C T



ABSTRACT

Two new zigzag 1-D polymeric Zn(II) coordination polymers {[Zn(L₁)($\mu_{1,5}$ -dca)](H₂O)}_n (1), {[Zn(L₂) ($\mu_{1,5}$ -dca)](ClO₄)}_n (2) of two potentially tridentate NNO-, NNN-, donor Schiff base ligands [2-(2-(4, 6-dimethylpyrimidin-2-yl)hydrazono)methyl)phenol] (L₁), [1-(4,6-dimethylpyrimidin-2-yl)-2-(dipyridin-2ylmethylene)hydrazine] (L₂) have been synthesized and characterized by elemental analyses, IR and ¹H NMR, fluorescence spectroscopy and single crystal X-ray crystallography. The dicyanamide ions act as linkers ($\mu_{1,5}$ mode) in the formation of these coordination polymers. Both the complexes 1 and 2 have same distorted square pyramidal geometry around the Zn(II) centres. The weak forces like $\pi \cdots \pi$, C–H $\cdots \pi$, anion $\cdots \pi$ interactions lead to various supramolecular architectures. Complex 1 shows high chelation enhanced fluorescence compared to that of 2. The fluorescence spectral changes observed high selectivity towards Zn(II) over other metal ions such as Mn(II), Co(II), Ni(II), Cu(II).

© 2015 Elsevier B.V. All rights reserved.

Introduction

The complexation of group 12 metal ions with polydentate Schiff base ligands is a well studied area of research in coordination chemistry [1–5]. These ligands have preparative accessibilities, structural variety and varied denticity, forming complexes of

* Tel.: +91 9804734352. E-mail address: saugata.konar@gmail.com

http://dx.doi.org/10.1016/j.molstruc.2015.02.048 0022-2860/© 2015 Elsevier B.V. All rights reserved. different coordination numbers and nuclearities with interesting molecular and crystalline architectures [6–16]. A substantial amount of work on pyridine and pyrazole derived Schiff base ligands have emerged in the literature, while works on pyrimidine derived Schiff base ligands are scarce. Pyrimidine derivatives play a dominant role in biological systems, the ring system being present in, for example, nucleic acids, several vitamins, co-enzymes and antibiotics [17–19]. Zinc is an essential element in the biosystem. It is required in genetic materials, DNA, RNA polymerases, the



CrossMark

regulatory Zn finger protein (structural motif for eukaryotic DNAbinding protein) in forming nucleic acids. The biological significance of Zn(II) has led to the development of numerous fluorescent chemo sensors [20].

It is well known that the careful selection of the organic ligands is one of the key factors for the synthesis of the coordination compounds with novel structures. The synthesis and investigation of new coordination polymers have been of great interest in the fields of crystal engineering and coordination chemistry because of their potential applications and intriguing architectures and topologies [21–24]. Over the last two decades, numerous spectacular coordination polymers have been reported, such as 1D-chains and ladders, 2D grids, and 3D microporous networks [25–30]. The selection of bridging ligand is one of the key steps for these types of syntheses.

In the present study (Scheme 1), two new zigzag 1-D polymeric Zn(II) coordination polymers $\{[Zn(L_1)(\mu_{1,5}-dca)](H_2O)\}_n$ (1), $\{[Zn(L_2)(\mu_{1,5}-dca)](ClO_4)\}_n$ (2) have been prepared by using pyrimidine derived tridentate NNO and NNN donor Schiff base ligands ([1 + 1] condensation products of 2-hydrazino-4,6-dimethyl pyrimidine with salicylaldehyde and di(2-pyridyl) ketone). My interest is to observe the metal ion coordination environments and photoluminescence using Zn(II) metal ion templates, the organic ligands L₁ and L₂, and suitable bridging units. In the complexes 1 and 2, the two Zn(II) centres are held together by $\mu_{1,5}$ -bridged dicyanamide ions. The fluorescence spectral changes observed high selectivity towards Zn(II) over other metal ions such as Mn(II), Co(II), Ni(II), Cu(II). The synthetic details, spectral

characterizations, X-ray crystal structures and fluorescence studies of **1** and **2** have reported here.

Experimental

Materials

All chemicals were of reagent grade, purchased from commercial sources and used without further purification. Di (2-pyridyl) ketone was purchased from Aldrich Chemical Company, USA and used without further purification.

Caution! Although we have not encountered any problems, it should be kept in mind that perchlorate compounds of metal ions are potentially explosive especially in the presence of organic ligands. Only a small amount of the material should be prepared and it should be handled with care.

Physical measurement

The infrared spectra of the complexes were recorded on a Perkin-Elmer RX I FT-IR spectrophotometer with KBr discs (4000–400 cm⁻¹). Elemental analyses (C, H, and N) were carried out using a Perkin-Elmer 2400 II elemental analyzer. ¹H NMR spectra were recorded on a Bruker 300 MHz FT-NMR spectrometer using trimethylsilane as an internal standard in d₆-DMSO for complex **1**, **2** and **3**. Steady state absorption and fluorescence spectra for all the three complexes and the Schiff base ligand were measured with a Hitachi UV/Vis U-3501 spectrophotometer and Perkin Elmer



LS50B fluorimeter, respectively at room temperature (298 K). All the spectral measurements were done at ${\sim}10^{-5}$ (M) concentration of solute in order to avoid aggregation and self quenching.

Synthesis of the ligands (L_1) and (L_2)

The ligand L_1 was synthesized and characterized using literature method [31].

L₁: ¹H-NMR, L₁ (d₆-DMSO, δ): δ 2.26 (6H, s, 4'-CH₃ and 6'-CH₃), 6.62 (1H, s, H-5'), 6.83 (1H, m, H-5), 6.84 (1H, d, *J* = 7.8 Hz, H-3), 7.18 (1H, t, *J* = 7.5 Hz, H-4), 7.32 (1H, d, *J* = 7.4 Hz, H-6), 8.19 (1H, s, H-7), 11.34 (1H, s, NH), 11.74 (1H, s, 2-OH). IR (KBr; v/cm⁻¹): 3247 (vN-H), 1620 (vC=C), 1566 (vC=NH), 885 (vC_{pym}-H), 1255 (vC-O).

The ligand L_2 was synthesized and characterized using literature method [30].

L₂: Yield: 3.13 g (85%); M.p.95 (°C) 152; Anal. Calc. for $C_{17}H_{16}N_6$: C, 69.86; H, 5.47; N, 28.76 Found: C, 69.81; H, 5.41; N, 28.30%. ¹H-NMR, L₂ (d₆-DMSO, δ): 2.34 (6H, s, 4″-CH₃ and 6″-CH₃), 6.78 (1H, s, 5″-H), 7.46 (1H, ddd, *J* = 8.0, 5.0, 1.5 Hz, H-5), 7.47 (1H, ddd, *J* = 8.0, 1.0, 1.0 Hz, H-3), 7.53 (1H, ddd, *J* = 8.0, 5.0, 1.5 Hz, H-5'), 7.94 (1H, ddd, *J* = 8.0, 1.5, 1.0 Hz H-3'), 7.96 (1H, ddd, *J* = 8.0, 8.0, 1.5 Hz, H-4'), 7.97 (1H, ddd, *J* = 8.0, 7.5, 1.5 Hz, H-4), 8.57 (1H, ddd, *J* = 5.0, 1.5, 1.0 Hz, H-6), 8.84 (1H, ddd, *J* = 5.0, 1.5, 1.0 Hz, H-6'). IR (KBr; v/ cm⁻¹): 3412(vN-H), 1528 (vC=N), 2920 (w) (vC-H), 1215 (ms), (vC=C), 1065 (m) (pym).

Preparation of complexes

Preparation of complex $[C_{15}H_{15}N_7O_2Zn]$ (1)

To a methanol solution (30 cm^3) of $\text{Zn}(\text{ClO}_4)_2$, $6\text{H}_2\text{O}$ (0.744 g, 2 mmol), a solution of the Schiff base L_1 in the same solvent (0.482 g, 2 mmol) was slowly added, followed by a solution of sodium dicyanamide (0.356 g, 4 mmol) in a minimum volume of aqueous methanol with constant stirring. The stirring was continued for another 2 h and filtered. The light yellow solution was kept in a refrigerator at 10 °C which produced yellow hexagonal crystals suitable for X-ray diffraction after 10 days. The crystals were isolated by filtration and air-dried. Yield: 61%. Anal. Calc. for C₁₅H₁₅N₇O₂Zn: C, 48.38; H, 3.49; N, 26.34; O, 4.30. Found: C, 48.25; H, 3.45; N, 26.14; O, 4.20. IR (KBr; v/cm⁻¹): 2345 (vsC = N + vas), 2193 (vsC = N), 1085 (ClO_4^-) . ¹H-NMR $(d_6$ -DMSO, δ): 2.31 (3H, s, 4'-CH₃), 2.38 (3H, s, 6'-CH₃), 6.45 (1H, t, *J* = 7.2 Hz, H-5), 6.63 (1H, br d, J = 8.4 Hz, H-3), 6.72 (1H, s, H-5'), 7.08 (1H, br d, J = 8.1 Hz, H-6), 7.15 (1H, br dd, J = 8.4, 7.2 Hz, H-5), 8.20 (1H, s, H-7), 12.13 (1H, s, NH).

Preparation of complex $[C_{19}H_{16}ClN_9O_4Zn]$ (2)

Complexes **2** was prepared by the same procedure as **1** using $Zn(ClO_4)_2 \cdot 6H_2O$ as metal precursor.

For complex **2**: Yield: 65.5%. Anal. Calc. For $C_{19}H_{16}ClN_9O_4Zn$ C, 42.61; H, 2.99; N, 23.55; O, 11.96. Found: C, 42.51; H, 2.91; N, 23.45; O, 11.86. IR (KBr; v/cm⁻¹): 2377 (vsC \equiv N + vas), 2188 (vsC \equiv N), 1081(ClO₄). ¹H-NMR, (d₆-DMSO, δ): 2.37 (3H, s), 2.46 (3H, s), 6.91 (1H, s), 7.60 (4H, m), 8.01 (2H, m), 8.61 (1H, br s), 8.85 (1H, br s).

Single crystal X-ray crystallography

Selected crystal data for **1** and **2** are given in Table 1 and selected metrical parameters of the complexes are given in Table 2. For complexes **1** data collections were made using Bruker SMART APEX II CCD area detector equipped with graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å) source in ω scan mode at 150(2) K. For complex **2**, data collection was made using

Table 1

Crystal data and refinement details of complexes for 1 and 2.

Compound	1	2
Empirical formula	C ₁₅ H ₁₃ N ₇ OZn	C ₁₉ H ₁₆ ClN ₉ O ₄ Zn
Formula weight	372.71	535.25
Temperature (K)	293	293
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Space group	P21	P-1
Unit cell dimensions		
a (Å)	8.1305(4)	7.646(5)
b (Å)	13.8732(7)	10.808(5)
c (Å)	8.7550(4)	14.140(5)
α (°)	90	107.141(5)
β (°)	112.459(2)	103.244(5)
γ (°)	90	93.554(5)
Volume (Å ³)	912.63(8)	1076.3(9)
Z	2	2
Density _{cal} (Mg m ⁻³)	1.356	1.652
Absorption coefficient (mm ⁻¹)	1.361	1.314
F(000)	380	544
Crystal size (mm ³)	$0.13 \times 0.15 \times 0.16$	$0.11 \times 0.14 \times 0.19$
Index ranges	$-9 \leqslant h \leqslant 10$	$-7\leqslant h\leqslant 7$
	$-17 \leqslant k \leqslant 17$	$-10 \leqslant k \leqslant 10$
	$-11 \leqslant l \leqslant 11$	$-12 \leqslant l \leqslant 14$
Independent reflections (R_{int})	281 [<i>R</i> (int) = .0452]	2186 [<i>R</i> (int) = 0.0311]
Absorption correction	Multi-scan	Multi-scan
Refinement method	Full-matrix least	Full-matrix least
	squares on F ²	squares on F^2
Data/restraints/parameters	2281, 1, 223	2186, 0, 309
Reflections collected	11,977	3463
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0334$	$R_1 = 0.2042$
	$wR_2 = 0.0882$	$wR_2 = 0.956$
Largest difference peak and hole (eÅ ⁻³)	-0.27 and 0.44	-0.57 and 0.78

Table 2	
Selected	bond distances (Å) and angles (°) in 1 and 2

Selecte	d bonds	Value (Å)	Select	ed angles		(°)
Comple	ex 1					
Zn1	-01	2.024(3)	01	-Zn1	—N1	86.43(12)
Zn1	-N1	2.068(2)	01	-Zn1	-N4	162.22(11)
Zn1	-N4	2.175(3)	01	-Zn1	-N5	95.79(16)
Zn1	-N5	2.035(4)	01	-Zn1	-N6	90.96(16)
Zn1	-N6	1.984(4)	N1	-Zn1	-N4	76.26(13)
			N1	-Zn1	-N5	116.89(16)
			N1	-Zn1	-N6	130.05(17)
			N4	-Zn1	-N5	95.64(15)
			N4	-Zn1	-N6	97.04(15)
			N5	-Zn1	-N6	113.01(17)
			Zn1	-N1	-N2	114.9(2)
Comple	ex 2					
Zn01	—N1	2.180(7)	N1	-Zn01	-N4	74.5(3)
Zn01	-N4	2.102(8)	N1	-Zn01	-N5	147.3(3)
Zn01	—N5	2.165(7)	N1	-Zn01	-N7	102.1(3)
Zn01	—N7	1.979(9)	N1	-Zn01	—N9	97.1(3)
Zn01	—N9	2.014(9)	N4	-Zn01	-N5	73.0(3)
			N4	-Zn01	-N7	129.3(3)
			N4	-Zn01	—N9	120.6(3)
			N5	-Zn01	—N7	95.9(3)
			N5	-Zn01	—N9	102.0(3)
			N7	-Zn01	—N9	110.1(4)

Bruker SMART APEX II CCD area detector area detector equipped with graphite monochromated Mo K α radiation (λ = 0.71073Å) source in ϕ and ω scan mode at 293(2) K. Cell parameters refinement and data reduction were carried out using Bruker SMART [32] and Bruker SAINT softwares for all the complexes. The structures were solved by direct and refined by full-matrix leastsquares based on F² using the SHELXS-97 and SHELXL-97 programs



Fig. 1. Molecular structure with atom numbering scheme of 1 (Asymmetric unit).



Fig. 2. Molecular structure with atom numbering scheme of 2 (Asymmetric unit).



Fig. 3. Polymeric 1D zigzag chain running along *a*-axis in 1 (H₂O molecules are omitted for clarity).



Fig. 4. Polymeric 1D zigzag chain along c-axis in 2 (perchlorate ions are omitted for clarity).

[33]. For **1** and **2** non hydrogen atoms were refined anisotropically till the convergence is attained. Better quality crystals for **2** could not be prepared after several trials.

Results and discussion

Synthesis

The ligand L_1 and L_2 were synthesized by the direct condensation reaction of 2-hydrazino-4,6-dimethyl pyrimidine with salicylaldehyde and di(2-pyridyl) ketone respectively, taken in methanol in 1:1 M proportion. The complexation behaviour of L_1 and L_2 towards Zn(II) metal salt were investigated. Complexes **1** and **2** were obtained by mixing the ligands and respective Zn(II) salts and sodium dicyanamide taken in 1:1:2 M ratio in methanol. X-ray quality crystals of **1** and **2** were obtained upon slow evaporation of the suitable reaction mixtures at room temperature.

Structural description

Description of structure of complexes 1 and 2

The Molecular structure of complexes **1** and **2** with atom numbering schemes are shown in Figs. 1 and 2 respectively. The structures of **1** and **2** consist of well isolated chains of Zn atoms bridged by dicyanamide ligands. The complexes 1 and 2 crystallize in space group P2₁ and P-1. The unit cell of **1** comprises of one molecule and that of **2** contains two molecules. The geometry around the Zn(II) centres may be described as distorted square pyramidal ($\tau = 0.44$ for **1** and 0.32 for **2**) [34]. The structure of **1** consists of the neutral mononuclear unit, $[Zn(L_1)(dca)](H_2O)$ in which the basal plane for 1 is formed by N4 from pyrimidine N atom, N1 from azomethine N atom, O1 from hydroxyl group, N5 from bridging dicyanamide and that of **2** consists of neutral mononuclear unit, $[Zn(L_2)(dca)_2](ClO_4)$ where the basal plane is formed by N1 from pyrimidine N atom, N4 from azomethine N atom, N5 from pyridine N atom, N9 from dicyanamide bridge. In both the complexes the axial positions are occupied by N atom from bridging dicyanamide (N7 for 1, N9 for 2). The Zn—N axial bond distances of 1.983 Å (for 1) and 1.979 Å (for 2) are different from that of the Zn–N distances in the basal planes of 1 and 2. The angle subtended at the Zn centre by the N atom of two bridging 1,5 dicyanamide anions is 113.01° and 110.07° for **1** and 2 and the distance between two Zn centres is 8.130 Å and 7.646 Å for 1 and 2. The NCN bent angle of the dicyanamide ligand is 128.30° and 132.22° for **1** and **2**. The Polymeric 1D zigzag chain of the coordination polymers of **1** and **2** has been shown in Figs. 3 and 4 respectively. It has been observed that the aromatic benzene ring, Cg3 (Cg3 = C1-C2-C3-C4-C5-C6) undergoes strong faceto-face $\pi \cdots \pi$ stacks (Fig. 5 and Table 3) with a pyrimidine ring,



Fig. 5. 2D supramolecular chain structure of complex 1 generated through the $\pi \cdots \pi$ along *c* axis (H₂O molecules are omitted for clarity).

Table 3 Geometric features (distances in Å and angles in degrees) of the $\pi \cdots \pi$ interactions obtained for **1**.

Complex	$Cg(Ring I) \cdots Cg(Ring J)$	Cg···Cg	Cg(I)· · · Perp	$Cg(J) \cdots Perp$	α	β	γ	Symmetry
Complex 1	$Cg(3) \cdots Cg(4)$	3.831(4)	3.746	3.820	15.22	4.23	12.03	−1 + X, Y, Z

 α = Dihedral angle between ring I and ring J (°); β = Cg(I) \rightarrow Cg(J) or Cg(I) \rightarrow Me vector and normal to plane I (°); γ = Cg(I) \rightarrow Cg(J) vector and normal to plane J (°); Cg–Cg = distance between ring Centroids (Å); CgI-··Perp = perpendicular distance of Cg(I) on ring J (Å); CgI-··Perp = Perpendicular distance of Cg(J) on ring I (Å); Cg(4) = centre of gravity of ring [C1–C2–C3–C4–C5–C6]; Cg(3) = centre of gravity of ring [N3–C8–N4–C12–C11–C10] for complex **1**.

Cg4 (Cg4 = N3–C8–N4–C12–C11–C10) leads to the formation of a 2D unit in **1**. In addition, each molecule of **1** is assembled by C–H··· π interactions (Fig. 6) involving the one C(methyl)–H group, C(9)–H(9B) donor group of pyrimidine ring and another aromatic benzene ring Cg(4) (Cg4 = C1–C2–C3–C4–C5–C6) of symmetry –X, 1/2 + Y, 1–Z (Table 4). In **2**, each molecule of **2** is assembled by C–H··· π interactions (Fig. 7) involving the one C(methyl)–H group, C(4)–H(4A) donor group of pyrimidine ring and another pyridine ring Cg(4) (Cg4 = N5–C8–C9–C10–C11–C12) of symmetry 1 – X, –Y, 1 – Z (Table 4). The non coordinating atoms O(3) of a dangling perchlorate anion is orientated towards the π -face (Fig. 8) of the pyridine ring Cg5 (Cg5 = N6–C13–C14–C15–C16–C17) in such an angle that it leads to three significant anion··· π interactions in **2** (Table 5).

Characterization of the ligands and the complex species

¹H NMR spectra

The structure of the ligands was well secured from their high resolution ¹H NMR spectra in DMSO- d_6 . The proton chemical shift assignments of the ligand L_1 given in the experimental section received support from observed coupling patterns and coupling constants involved therein. A part of the spectrum was typical of the presence of unsymmetrically substituted 1, 2-disubstituted benzene moiety. The upfield signal at δ 6.84 (1H, d, *J* = 7.8 Hz) in L_1 was typical of an aromatic proton (H-3) ortho to a phenolic hydroxyl. The same signal was coupled to H-4 resonance (δ 7.18, 1H, t, *J* = 7.5 Hz) and the latter was again coupling to a signal at δ 6.83 (1H, m, H-3) which was in turn coupled to a resonance at δ



Fig. 6. 2D supramolecular chain structure of complex **1** generated through the C–H \cdots π along *c* axis.

Table 4

Geometric features (distances in Å and angles in degrees) of the C–H $\cdots\pi$ interactions obtained for 1 and 2.

Complexes	$C-H\cdots Cg(Ring)$	H···Cg (Å)	C—H···Cg (°)	C···Cg (Å)	Symmetry
Complex 1	C9—H9B···Cg(4)	2.82	128	3.492(9)	−X, 1/2 + Y, 1 − Z
Complex 2	C4—H4A···Cg(4)	2.88	126	3.528(11)	1 − X, −Y, 1 − Z

For complex 1, Cg(4) = centre of gravity of ring [C1-C2-C3-C4-C5-C6] and for complex 2, Cg(4) = centre of gravity of ring [N5-C8-C9-C10-C11-C12].

7.32 (1H, br d, I = 7.4 Hz) for H-6. A sharp singlet at δ 8.19 (1H) was in consonance with the presence of the -CH=N- proton while that at δ 6.62 (1H, s) was commensurate with the presence of H-5 proton in 4,6-dialkylpyrimidine unit. The appearance of two aromatic methyls at the same position (δ 2.26, 6H, s) was in line with the presence of a locally symmetric 2-pyrimidyl unit. There were also a pair of low field signals at δ 11.34 (1H, br s) and 11.74 (1H, br s) for arylhydrazone NH and chelated phenolic OH protons. The 500 MHz ¹H spectrum of ligand L_2 in DMSO- d_6 displayed singlet signals at δ 2.26 (6H) and 6.80 (1H) which were quite similar to that of L₁ in respect of the 4, 6-dimethyl-2-pyrimidyl unit present therein. The signals at δ 8.58 (1H, ddd, J = 5.0, 1.5, 1.0 Hz) and 8.84 (1H, ddd, J = 5.0, 1.5, 1.0 Hz) with low J_0 value in L₂ were typical of α -proton resonance in pyridine system and thus assigned to H-6 and H-6', respectively. In the complex **1** of L_1 with Zn(II) salt and $N(CN)_2^-$ there were six sets of signals for protons on sp² hybridised carbon as in parent ligand L₁ but upfield shift of aromatic protons H-3, H-5 and H-6 were noticed in the complex. Again, the aromatic methyls are now nonequivalent because of coordination of pyrimidine nitrogen with Zn and consequently appearing at different positions (δ 2.31 and 2.38, 3H each, br s). It is noteworthy, that solution phase ¹H NMR spectral studies of the complexes **2** adduced for their similarity in the nature of coordination of L₂ to Zn (II). It was observed that H-3, H-5, H-6 and 4"-CH₃ experienced downfield shift upon coordination of metal with pyridine nitrogen.

Infrared spectra

The infrared spectra of the complexes are consistent with the structural data given in this paper. Complexes **1** and **2** exhibit strong absorption bands in the region 2345–2140 cm⁻¹ that correspond to $v_{C=N}$ modes for dca groups, attributed to $v_{as} + v_{s(C=N)}$ combination modes, $v_{as(C=N)}$ and $v_{s(C=N)}$. The shift towards higher wave numbers for the peaks of dca in **1** and **2** when compared to those of free dicyanamide is consistent with the coordination of dca in the complexes. These three bands appear at 2344, 2239, 2193 cm⁻¹ for complex **1**, at 2377, 2237, 2188 cm⁻¹ for complex **2** [35]. The strong $v_{C=N}$ azomethine bands occurring at 1608, 1597 for **1** and **2** respectively are shifted considerably towards



Fig. 7. C–H··· π interaction along *b*-axis in **2** (perchlorate ions are omitted for clarity).

lower frequencies compared to that of the free Schiff base ligands (1635 cm⁻¹), indicating coordination of the imino nitrogen atom [36].

Emission properties

The emission spectra of the Schiff base ligands L₁, L₂ and their Zn(II) complexes (1 and 2) were recorded at room temperature (298 K) in methanol solvent by exciting at the absorption maxima of the ligands (Fig. 9). In both the cases, L₁ and L₂ have low fluorescence intensity with emission maxima at \sim 433 nm and \sim 420 nm, respectively, whereas, the metal complexes show red shifted enhanced fluorescence emission with maxima at ~456 nm for complex 1 and 526 nm for complex 2 (Table 3). The low emission intensity of the ligand may be due to occurrence of photo induced electron transfer processes in the presence of lone pairs of electrons of the donor atoms within it [37]. The enhancement of emission intensity of Zn(II) and Cd(II) complexes is probably due to the metal ligand chelation [38] or increase in conformational rigidity of the ligands upon complexation [39]. In the present study, the addition of different metal ions (Ni⁺², Co⁺², Mn⁺², Cu⁺², Cd⁺², Zn⁺²) to a 1:1 mixture of L₁ and dicyanamide in methanol indicates that it is

the Zn^{+2} ion which show high selectivity compared to other metal ions (Fig. 10).

Conclusion

The pyrimidine derived NNO and NNN donor Schiff base ligands L_1 and L_2 along with $\mu_{1,5}$ bridging dicyanamide ions form 1D polymeric zigzag chains of Zn(II) complexes **1** (with L_1), **2** (with L_2). In all the complexes, two zinc complexes have square pyramidal environment around the metal centres. The ligands are fluorescence silent but the Zn(II) complex of L_1 i.e. complex **1** shows highest chelation enhanced flourescene compared to the Zn(II) complexes of L₂ i.e. complex 2. It seems interesting to conduct a systematic study on a designed series of transition metal complexes with the intention to understand the way in which different supramolecular interactions cooperate and direct the supramolecular assembly of the molecular building blocks with variation in the ligand moieties. Fluorescence silent behaviour of the ligand may probably be due to the presence of non bonding electron pairs on its nitrogen and oxygen donors (for L₁) and nitrogen donors (for L₂). These electrons are involved in coordinate bond formation with metal ions during complexation. During metal



Fig. 8. Anion-pi interaction in complex 2 along *b* axis.

Table 5

Geometric features (distances in Å and angles in degrees) of the anion $\cdots \pi$ interactions obtained for **2**.

Complex	$Y - X \cdots Cg(J)$	$X{\cdots}Cg(J)$	$Y \! \cdots \! Cg(J)$	$\angle Y - X \cdots Cg(J)$	X—Perp
Complex 2	$Cl1-O3\cdots Cg(5)^{a}$	3.400(14)	4.148(6)	112.4(7)	3.329

For complex **2**, Cg(5) = centre of gravity of ring [N6–C13–C14–C15–C16–C17]. ^a Symmetry element: 1 – X, –Y, 1 – Z.







Fig. 10. Fluorescence emission (10^{-4} M) in the presence of L₁, Ni²⁺, Co²⁺, Mn²⁺,Cu²⁺,Cu²⁺,Cd²⁺ and complex 1 (from bottom to top in CH₃OH).

binding process, non radiative channels and flexible bonds are inactive due to strong binding. This strong binding of the ligand L_1 using its N, O donors with comparatively harder Zn(II) may be the reason for chelation enhanced fluorescence of **1** compared to **2** of L_2 having only N donor atoms.

Appendix A. Supplementary data

CCDC 861097 and 855076 contain the supplementary crystallographic data for 1 and 2. These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Acknowledgements

S. Konar acknowledges the financial support provided by University Grants Commission, India (Award letter No. F.4-2/ 2006(BSR)/13-1089/2013(BSR), dated September, 2013) through the Dr. D. S. Kothari Post Doctoral Fellowship (DSKPDF). S. Konar specially thanks to Prof. S. Mukhopadhyay, Department of Chemistry, Jadavpur University and Prof. S. K. Kar, Department of Chemistry, University of Calcutta, Kolkata, India.

References

- [1] M.B. Davis, Coord. Chem. Rev. 164 (1997) 27-160.
- [2] D.R. Smith, Coord. Chem. Rev. 172 (1998) 457–573.
- [3] A.D. Garnovskii, A.L. Nivorozhkin, V.I. Minkin, Coord. Chem. Rev. 126 (1993) 1– 69.
- [4] V. Alexander, Chem. Rev. 95 (1995) 273-342.
- [5] P.A. Vigato, S. Tamburini, L. Bertolo, Coord. Chem. Rev. 251 (2007) 1311–1492.
 [6] D. Braga, F. Grepioni, A.G. Orpen, Cryst. Eng.: From Mole. Cryst. Mater. 538 (1999) 89–106.
- [7] P. Comba, P.W. Hambley, Molecular Modelling of Inorganic and Coordination Compounds, second ed., VCH, Weinheim, 2001. pp. 161–162.
- [8] K.-M. Dethlefs, P. Hobza, Chem. Rev. 100 (2000) 143-168.
- [9] L. Brammer, Chem. Soc. Rev. 33 (2004) 476–489.

- [10] C. Janiak, Coord. Chem. Rev. 250 (2006) 66–94.
- [11] J.G. Planas, C. Masalles, R. Sillanpaa, R. Kivekas, F. Teixidor, C. Vinas, Cryst. Eng. Commun. 8 (2006) 75–83.
- [12] M.K. Milčič, V.B. Medakovic, D.N. Sredojevic, N.O. Juranic, S.D. Zaric, Inorg. Chem. 45 (2006) 4755–4763.
 - [13] M.J. Zaworotko, Cryst. Growth Des. 7 (2007) 4-9.
 - [14] G.A. Hembury, V.V. Borovkov, Y. Inoue, Chem. Rev. 108 (2008) 1–73.
 - [15] Q. Ye, D.-W. Fu, H. Tian, R.-G. Xiong, P.W.H. Chen, S.D. Huang, Inorg. Chem. 47 (2008) 772–774.
 - [16] X.-H. Chen, Q.-J. Wu, Z.-Y. Liang, C.-R. Zhan, J.-B. Liu, Acta Crystallogr. Sect. C 65 (2009) 190–194.
 - [17] W.G. Rice, J.A. Turpin, C.A. Schaeffer, L. Graham, D. Clanton, R.W. Buckheit Jr., D. Zaharevitz, M.F. Summers, A. Wallqvist, D.G. Covell, J. Med. Chem. 39 (1996) 3606–3616.
 - [18] M. Otsuka, M. Fujita, Y. Sugiura, J. Med. Chem. 37 (1994) 4267-4269.
 - [19] F. Zamora, M. Kunsman, M. Sabat, B. Lippart, Inorg. Chem. 36 (1997) 1583– 1587.
 - [20] E.L. Que, D.W. Domille, C.J. Chang, Chem. Rev. 108 (2008) 1517–1549.
 - [21] R.-F. Song, Y.-B. Xie, J.-R. Li, X.-H. Bu, CrystEngComm 7 (2005) 249–254.
 - [22] R. Peng, T. Wu, D. Li, CrystEngComm 7 (2005) 595-598.
 - [23] G. Li, Y. Xing, S. Song, N. Xu, X. Liu, Z. Su, J. Solid State Chem. 181 (2008) 2406-
 - 2411. [24] H. Yang, X. Meng, Y. Liu, H. Hou, Y. Fan, X. Shen, J. Solid State Chem. 181 (2008)
 - 2178–2184. [25] C.-Q. Zhao, M.C. Jennings, R.J. Puddephatt, J. Inorg. Organomet. Polym. 18 (2008) 143–148.
 - [2008] 143–146.
 [26] W.-W. Dong, J. Zhao, L. Xu, J. Solid State Chem. 181 (2008) 1149–1154.
 - [27] Z. Chen, X. Li, F. Liang, J. Solid State Chem. 181 (2008) 2078–2086.
 - [28] H.L. Gao, L. Yi, B. Zhao, X.Q. Zhao, P. Cheng, D.Z. Liao, S.P. Yan, Inorg. Chem. 45 (2006) 5980–5988.
 - [29] B.L. Chen, F.R. Fronczek, A.W. Maverick, Inorg. Chem. 43 (2004) 8209-8211.
 - [30] S. Konar, Inorg. Chem. Commun. 49 (2014) 76–78.
 - [31] S. Gupta, S. Pal, A. Barik, A. Hazra, S. Roy, T.N. Mandal, S.M. Peng, G.H. Lee, M.S.El. Fallah, J. Tercero, S.K. Kar, Polyhedron 27 (2008) 2519–2528.
 - [32] Bruker, SMART v5.631, Bruker AXS Inc., Madison, WI, USA, 2001.
 - [33] G.M. Sheldrick, SHELXS-97 and SHELXL-97, University of Göttingen, Göttingen, Germany, 1997.
 - [34] S. Konar, A. Jana, K. Das, S. Ray, S. Chatterjee, J.A. Golen, A.L. Rheingold, S.K. Kar, Polyhedron 30 (2011) 2801–2808.
 - [35] S.R. Marshall, A.L. Rheingold, L.N. Dawe, W.W. Shum, C. Kitamura, J.S. Miller, Inorg. Chem. 41 (2002) 3599–3601.
 - [36] L. Xue, Q. Liu, H. Jiang, Org. Lett. 11 (2009) 3454-3457.
 - [37] S. Basak, S. Sen, S. Banerjee, S. Mitra, G. Rosair, M.T.G. Rodriguez, Polyhedron 26 (2007) 5104–5112.
 - [38] D.X. West, A.A. Nassar, Transition Met. Chem. 23 (1998) 321-325.
 - [39] S. Chattopadhyay, K. Bhar, S. Das, S. Satapathi, H.K. Fun, P. Mitra, B.K. Ghosh, Polyhedron 29 (2010) 2041–2047.