Syntheses, structures and luminescence behaviour of some zinc(II) complexes containing acetate and tetradentate Schiff bases

ASHIS KUMAR MAJI, SUBHASIS ROY, SOMNATH CHOUBEY, RAJARSHI GHOSH* and BARINDRA KUMAR GHOSH*

Department of Chemistry, The University of Burdwan, Burdwan 713 104, India
e-mail: rajarshi_chem@yahoo.co.in; barin_1@yahoo.co.uk

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Abstract. Two mononuclear compounds of the types pentacoordinated $[\text{Zn}(\text{L1})(\text{OAc})]\text{PF}_6 \cdot \text{H}_2\text{O}$ (**1**) and hexacoordinated $[\text{Zn}(\text{L2})(\text{OAc})]\text{PF}_6$ (**2**) [$\text{L1} = \text{N,N}'$ -(bis(pyridin-2-yl)formylidene)-1,3-propanediamine; $\text{L2} = \text{N,N}'$ -(bis(pyridin-2-yl)benzylidene)-1,4-butanediamine] have been synthesized using one-pot reactions of a 1:1:1 molar ratio of $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$, L1/L2 , ammonium hexafluorophosphate in MeOH at room temperature. Compounds **1** and **2** are characterized on the basis of microanalytical, spectroscopic, thermal and other physicochemical results. Single crystal X-ray structural study reveals that the zinc(II) centre in **1** is coordinated by four N atoms of the Schiff base L1 and one O atom of terminal acetate with a ZnN_4O chromophore, whereas in **2**, the zinc(II) centre is bound by four N atoms of the tailored Schiff base L2 and two O atoms of the chelated acetate. In the crystalline state, mononuclear units in **1** are engaged in weak cooperative intermolecular $\text{O} \cdots \text{H} \cdots \text{O}$ and $\text{C} \cdots \text{H} \cdots \text{F}$ hydrogen bonds affording a 1D chain. The individual units of **2** are packed by $\pi \cdots \pi$ and anion $\cdots \pi$ interactions to form a 2D sheet structure. The complexes show reasonable thermal stabilities and display intraligand $\pi \rightarrow \pi^*$ fluorescence in solid state at room temperature.

Keywords. Mononuclear zinc(II); Schiff base; versatile acetate; X-ray structure; luminescence.

1. Introduction

The study of mono-, di-, and polynuclear complexes of zinc(II) has been the centre of current research because of their interesting synthetic, structural, spectroscopic and optoelectronic features^{1–4} and biological aspects.⁵ The essential prerequisites for such work are the judicious choice⁶ of organic spacers and inorganic/organic terminals/bridges that may lead to directed molecular properties. Recently, we got interested^{7–11} in the construction of different coordination molecules through variation of ligand backbones and metal ion coordination environments. In this regard, Schiff base spacers and pseudohalide terminals/bridges have been widely used. Schiff bases^{12,13} are useful chelators because of their ease of preparation, structural varieties, varied denticities and subtle steric and/or electronic control on their frameworks. Carboxylate like acetate is known to have different varieties of ligational motifs affording interesting molecular aggregates and crystalline architectures coupled with different physico-chemical properties.^{14–20} Earlier we reported^{16,18} some mono- and dinuclear copper(II) and nickel(II) acetate complexes in combination with a tailored diimine and a tailored Schiff base with interesting molecular and crystalline architectures coupled with ferromagnetic and luminescent

properties. The present work stems from our interest to build new molecular and crystalline aggregates of zinc(II) acetates in combination with two Schiff bases viz. $\text{N,N}'$ -(bis(pyridin-2-yl)formylidene)-1,3-propanediamine (L1) and $\text{N,N}'$ -(bis(pyridin-2-yl)benzylidene)-1,4-butanediamine (L2) (scheme 1). We have successfully isolated two mononuclear complexes $[\text{Zn}(\text{L1})(\text{OAc})]\text{PF}_6 \cdot \text{H}_2\text{O}$ (**1**) and $[\text{Zn}(\text{L2})(\text{OAc})]\text{PF}_6$ (**2**). The details of synthesis, characterization, structure and properties of **1** and **2** are described below.

2. Experimental

2.1 Materials

High purity 1,3-propanediamine (Spectrochem, India), 1,4-butanediamine (Lancaster, UK), 2-benzoylpyridine (Lancaster, UK), zinc(II) acetate (E. Merck, India) and ammonium hexafluorophosphate (Fluka, Germany) were purchased from respective concerns and used as received. The Schiff base, $\text{N,N}'$ -(bis(pyridin-2-yl)benzylidene)-1,3-propanediamine (L1)/ $\text{N,N}'$ -(bis(pyridin-2-yl)benzylidene)-1,4-butanediamine (L2) was prepared by condensation of 1:2 molar ratio of 1,3-propanediamine/1,4-butanediamine and 2-benzoylpyridine using the

Scheme 1. Frameworks of L1 and L2.

reported method.^{17,21} All other chemicals and solvents used were AR grade.

2.2 Physical measurements

Elemental analyses were performed on a Perkin-Elmer 2400 CHNS/O elemental analyzer. Molar conductance were measured using a Systronics conductivity meter where the cell constant was calibrated with 0.01(M) KCl solution, and dry MeCN was used as solvent. IR spectra (KBr discs, 4000–400 cm^{-1}) were recorded using a Perkin-Elmer FTIR model RX1 spectrometer. Thermal behaviour were examined with a Perkin-Elmer Diamond TG/DT analyzer heated from 35–740°C under nitrogen. Ground state absorption spectra were measured with a Jasco model V-530 UV-Vis spectrophotometer. Solid state fluorescence measurements were done using a Hitachi Fluorescence Spectrofluorimeter F-4500.

2.3 Isolation of the complexes $[\text{Zn}(\text{L1})(\text{OAc})]\text{PF}_6 \cdot \text{H}_2\text{O}$ (**1**) and $[\text{Zn}(\text{L2})(\text{OAc})]\text{PF}_6$ (**2**)

To a methanolic solution (10 mL) of $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (0.022 g, 0.1 mmol), L1 (0.04 g, 0.1 mmol) taken in the same solvent (10 mL) was added dropwise. To this resulting solution mixture, a methanolic solution (5 mL) of NH_4PF_6 (0.018 g, 0.1 mmol) was added as source of counter anion. The colourless reaction mixture was kept in an open air for slow evaporation. After a week colourless crystals of **1** were collected and dried in vacuo over silica gel indicator. Yield: 0.498 g (72%). Complex **2** was prepared similarly using the same reaction stoichiometry and reaction condition as in **1** except that methanolic solution (10 mL) of L2 (0.042 g, 0.1 mmol) instead of L1 was added to the reaction mixture. Yield: 0.516 g (75%). Anal. Calc. for $\text{C}_{29}\text{H}_{29}\text{N}_4\text{O}_3\text{F}_6\text{PZn}$ (**1**): C, 50.3; H, 4.2; N, 8.1 Found: C, 50.1; H, 3.9; N, 8.3%. IR (KBr, cm^{-1}): $\nu(\text{O-H})$ 3422; $\nu(\text{C=N} + \text{C=C})$ 1633, 1593; $\nu_{\text{as}}(\text{COO}^-)$ 1571; $\nu_{\text{s}}(\text{COO}^-)$ 1334; $\nu(\text{PF}_6^-)$ 836, 557; UV-Vis [MeCN, $\lambda_{\text{max}}/\text{nm}$ (ϵ , $\text{M}^{-1} \text{cm}^{-1}$): 282 (4.72×10^3), Λ_{M} (MeCN, $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$): 115. Anal. Calc. for $\text{C}_{30}\text{H}_{29}\text{N}_4\text{O}_2\text{F}_6\text{PZn}$ (**2**): C, 52.3; H, 4.3; N, 8.1. Found:

C, 52.6; H, 4.1; N, 7.9%. IR (KBr, cm^{-1}): $\nu(\text{C=N} + \text{C=C})$ 1627, 1590; $\nu_{\text{as}}(\text{COO}^-)$ 1578; $\nu_{\text{s}}(\text{COO}^-)$ 1329; $\nu(\text{PF}_6^-)$ 842, 557; UV-Vis [MeCN, $\lambda_{\text{max}}/\text{nm}$ (ϵ , $\text{M}^{-1} \text{cm}^{-1}$): 28 (17.04×10^3), Λ_{M} (MeCN, $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$): 110.

2.4 X-ray crystallographic analyses

Single crystals of **1** and **2** suitable for X-ray analyses were selected from those obtained by slow evaporation of methanolic solutions at room temperature. Diffraction data were collected on a Bruker SMART CCD area-detector diffractometer using graphite monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). Intensity data were reduced using SAINT²² and the empirical absorption corrections were performed with SADABS²³ program. The structures were solved by SHELXS-97²⁴ and refined by full-matrix least-squares methods based on $|F|^2$ using the program SHELXL-97.²⁴ All non-hydrogen atoms were refined with anisotropic displacement parameters whereas hydrogen atoms were located geometrically and refined using a standard riding model. Materials for publication were prepared using PLATON²⁵ and Mercury 3.1²⁶ programs. F8 atom of the hexafluorophosphate group in **1** is in disordered state with occupancy factors of 0.6% (F8A) and 0.4% (F8B). A summary of the crystallographic data and structure determination parameters for **1** and **2** is given in table 1.

3. Results and Discussion

3.1 Synthesis and formulations

The penta- and hexacoordinated mononuclear compounds were isolated as single crystals through one-pot synthesis of 1:1 molar ratio of zinc(II) acetate, tetradentate Schiff bases (L1/L2) and ammonium hexafluorophosphate in methanolic solution at room temperature. The new complexes were characterized using microanalytical (C, H and N), spectroscopic, thermal and other physicochemical results. The microanalytical data are in good agreement with formulations **1** and **2**. The moisture-insensitive complexes are stable over a long period of time and soluble in common organic

Table 1. Crystal data and structure refinement for **1** and **2**.

Crystal parameters	1	2
Empirical formula	C ₂₉ H ₂₉ N ₄ O ₃ F ₆ PZn	C ₃₀ H ₂₉ N ₄ O ₂ F ₆ PZn
Formula weight	691.89	687.91
Crystal system	Orthorhombic	Monoclinic
Space group	Pbca	P2 ₁ /n
<i>a</i> (Å)	15.1451(3)	9.6828(2)
<i>b</i> (Å)	15.1703(3)	24.6511(6)
<i>c</i> (Å)	26.1615(5)	13.6654(3)
α (°)	90.00	90.00
β (°)	90.00	110.501(2)
γ (°)	90.00	90.00
<i>V</i> (Å ³)	6010.8(2)	3055.23(12)
λ (Å)	0.71073	0.71073
ρ_{calcd} (g cm ⁻³)	1.489	1.496
<i>Z</i>	8	4
Crystal size (mm ³)	0.20 × 0.11 × 0.06	0.22 × 0.08 × 0.05
Temperature (K)	296(2)	296(2)
μ (mm ⁻¹)	0.941	0.928
<i>F</i> (000)	2752	1408
θ ranges (°)	2.05 to 27.30	1.79 to 27.12
<i>h</i> / <i>k</i> / <i>l</i>	−19/19, −19/18, −33/33	−12/12, −31/31, −17/17
Reflections collected	91278	39989
Independent reflections (<i>R</i> _{int})	6716	6703
Data/restraints/parameters	6716/12/443	6703/0/398
Goodness-of-fit on <i>F</i> ²	1.056	0.997
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> = 0.0481 and w <i>R</i> = 0.1391	<i>R</i> = 0.0512 and w <i>R</i> = 0.1336
<i>R</i> indices (all data)	<i>R</i> = 0.0865 and w <i>R</i> = 0.1729	<i>R</i> = 0.1211 and w <i>R</i> = 0.1871
Largest diff. peak and hole (eÅ ⁻³)	0.675 and −0.450	0.518 and −0.554

Weighting scheme: $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$, $wR = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$, $\text{calcd } w = 1/[\sigma^2(F_o^2) + (xP)^2 + yP]$; $x = 0.0903$ (for **1**), 0.1000 (for **2**) and $y = 2.9010$ (for **1**), 0.0000 (for **2**), where $P = (F_o^2 + 2F_c^2)/3$.

Figure 1. Fluorescence spectra of (a) L1 and **1**; (b) L2 and **2** in MeCN solutions at room temperature.

solvents like MeOH, MeCN, DMF and DMSO, but are insoluble in water. In MeCN solutions, both the compounds show 1:1 electrolytic behaviour²⁷ as reflected in their low Λ_M values (**1**: 115 ohm⁻¹ cm² mol⁻¹; **2**: 110 ohm⁻¹ cm² mol⁻¹).

3.2 Spectroscopic studies

In IR spectra, Schiff bases L1 and L2 in the metal bound state exhibit $\nu(\text{C}=\text{N})$ plus $\nu(\text{C}=\text{C})$ stretching vibrations at ~ 1630 and ~ 1590 cm⁻¹. A strong absorption

Figure 2. Solid state fluorescence spectra of **1** and **2** at room temperature.

Figure 3. Molecular structure of $[\text{Zn}(\text{L1})(\text{OAc})]\text{PF}_6 \cdot \text{H}_2\text{O}$ in **1** with atom numbering schemes.

at 3422 cm^{-1} for $\nu(\text{O-H})$ observed in case of **1** and absent in **2** strongly suggests the presence of water molecule in the former. The stretching frequencies $\nu_{\text{as}}(\text{COO}^-)$ and $\nu_{\text{s}}(\text{COO}^-)$ of acetate group are seen at ~ 1570 and $\sim 1330\text{ cm}^{-1}$, respectively. The presence of hexafluorophosphate at ~ 840 and $\sim 560\text{ cm}^{-1}$ indicates counter anionic view with no metal coordination.²⁸ In MeCN solutions, complexes **1** and **2** show absorptions

Figure 4. ORTEP of $[\text{Zn}(\text{L2})(\text{OAc})]\text{PF}_6$ (**2**) with atom numbering schemes.

Table 2. Selected bond distances ($\text{\AA}$) for **1** and **2**.

Bond distances for 1		Bond distances for 2	
Zn1-N1	2.143(3)	Zn1-N1	2.108(4)
Zn1-N2	2.137(3)	Zn1-N2	2.143(3)
Zn1-N3	2.160(3)	Zn1-N3	2.144(3)
Zn1-N4	2.117(3)	Zn1-N4	2.101(3)
Zn1-O1	1.953(3)	Zn1-O1	2.471(5)
C27-O1	1.266(5)	Zn1-O2	2.080(4)
C27-O2	1.225(5)	C29-O1	1.238(6)
		C29-O2	1.250(6)

Table 3. Selected bond angles ($^\circ$) for **1** and **2**.

Bond angles for 1		Bond angles for 2	
N1-Zn1-N2	76.46(10)	N1-Zn1-N2	77.52(13)
N1-Zn1-N3	147.36(12)	N1-Zn1-N3	92.03(13)
N1-Zn1-N4	99.79(10)	N1-Zn1-N4	112.35(13)
N2-Zn1-N3	85.18(11)	N2-Zn1-N3	168.69(14)
N2-Zn1-N4	138.12(11)	N2-Zn1-N4	101.83(13)
N3-Zn1-N4	76.27(10)	N3-Zn1-N4	77.97(13)
O1-Zn1-N1	107.43(11)	O1-Zn1-N1	98.48(13)
O1-Zn1-N2	104.18(12)	O1-Zn1-N2	87.79(14)
O1-Zn1-N3	103.08(12)	O1-Zn1-N3	98.14(13)
O1-Zn1-N4	116.37(11)	O1-Zn1-N4	148.97(13)
O1-C27-O2	123.3(4)	O2-Zn1-N1	153.61(14)
		O2-Zn1-N2	92.45(14)
		O2-Zn1-N3	98.85(14)
		O2-Zn1-N4	93.48(14)
		O1-Zn1-O2	56.34(14)
		O1-C29-O2	122.0(5)

at 282 and 280 nm, respectively assignable to ligand-based transition.²⁹ The reflectance [**1**: λ , 280 nm; **2**: λ , 278 nm] in Nujol and electronic spectrum in MeCN for

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

Compound	D-H...A	D-H	H...A	D...A	D-H...A	Symmetry codes
1	O6-H119...O2	0.85(8)	1.97(9)	2.815(6)	170(9)	—
	C14A-H14B...F1	0.9700	2.5200	3.248(9)	131.00	1-x, -y, 1-z

Figure 5. 1D chain structure in **1** formed through O-H...O and C-H...F hydrogen bonds along crystallographic *c*-axis.**Table 5.** $\pi \cdots \pi$ Interaction parameter (Å, °) for **2**.

Cg-Cg	Cg-Cg distance	Dihedral angle (<i>i, j</i>)	Perpendicular distances between baricentres (<i>i, j</i>)	Slippage	Symmetry codes
Cg4...Cg4	5.297(3)	0.00	4.829(2)	2.178	1-x,2-y,1-z
Cg4...Cg4	4.567(3)	0.00	3.893(2)	2.389	2-x,2-y,1-z
Cg6...Cg6	5.592(4)	0.00	2.866(2)	4.802	2-x,2-y,2-z

Cg4: N(2)-C(2)-C(6)-C(5)-C(4)-C(3) and Cg6: C(7)-C(8)-C(9)-C(10)-C(11)-C(12)

Table 6. Anion... π interactions donor/acceptor scheme (Å, °) for **2**.

X-D...A	X-D	D...A	X...A	X-D...A	Symmetry code
P1-F6...Cg5	1.562(3)	3.414(4)	4.459(2)	122.9(2)	-1/2+x, 3/2-y, -1/2+z

Cg5: N(4)-C(18)-C(22)-C(21)-C(20)-C(19)

each complex are akin reflecting similar gross geometric structure and electronic structure in solid state and in solution. The photoluminescence behaviours of the ligands (L1 and L2) and the compounds **1** and **2** were examined in MeCN solutions and the compounds in the solid state at room temperature (298 K). As the Schiff base L1 was isolated in the form of a gummy mass, its fluorescence behaviour could not be measured in solid state. The spectral patterns are shown in figure 1. In MeCN solution, free L1 exhibits a broad fluorescent emission centred at 365 nm along with a weak emission at 330 nm (figure 1) upon excitation at the corresponding absorption band (274 nm). The corresponding compound **1** shows emission bands at the same wavelength

with higher intensity when excited at 282 nm. L2 shows emission at 310 nm upon photoexcitation at 278 nm in MeCN solution. Compound **2** shows emission bands at the same wavelength with higher intensity when excited at 280 nm. Upon photoexcitation at the corresponding absorption band 280 nm, solid sample of compound **1** containing L1 shows emission at 392 nm (figure 2). In our earlier study we have reported that L2 shows emission at 423 nm³⁰ upon excitation at 280 nm in the solid state. Solid sample of compound **2** shows luminescence at 405 nm upon photoexcitation at 280 nm. The luminescence in **1** and **2** in solid state as well as in MeCN solutions may be attributed to the intraligand (π - π^*) emission.^{10,11,31}

3.3 Molecular and crystalline structures of $[\text{Zn}(\text{L1})(\text{OAc})]\text{PF}_6 \cdot \text{H}_2\text{O}$ (**1**) and $[\text{Zn}(\text{L2})(\text{OAc})]\text{PF}_6$ (**2**)

ORTEP plots with atom numbering schemes of **1** and **2** are shown in figures 3 and 4, respectively. Selected bond lengths and angles pertaining to the coordination spheres of both the compounds are set in tables 2 and 3. Structural analysis reveals that the asymmetric unit in **1/2** consists of mononuclear species $[\text{Zn}(\text{L1/L2})(\text{OAc})]\text{PF}_6 \cdot n\text{H}_2\text{O}$ [$n = 1$ for **1** and $n = 0$ for **2**] (figures 3 and 4) with or without lattice water. The coordination polyhedron around zinc(II) in **1** is best described as a distorted square pyramid ($\tau = 0.15$)³² with a ZnN_4O chromophore whereas zinc(II) centre in **2** adopts a distorted octahedral geometry with a ZnN_4O_2 chromophore. Two pyridine N atoms (N1 and N4) and two imine N atoms (N2 and N3) of the Schiff base (L1) complete the basal plane whereas the apical position is occupied by the O1

Figure 6. 2D sheet structure in **2** formed through $\pi \cdots \pi$ and anion $\cdots \pi$ interactions along crystallographic ab -plane.

atom of the terminal acetate group (OAc). The core Zn1 atom is deviated by 0.67 Å from the basal plane consisting of the four N atoms (N1,N2,N3,N4) of the Schiff base. The smaller Zn-O(OAc) bond distance [1.953(3) Å] in **1** over the average Zn-N(Schiff base) distance [2.139(8) Å] is indicative of the stronger coordination of the anionic O atom of OAc over the neutral N-atoms (N1 N2, N3 and N4) of the Schiff base. The propylenic arm of L1 is to some extent puckered and the central carbon atom of the arm is in a disordered state with occupancy factor of 0.75% (C14A) and 0.25% (C14B).

In the crystal structure of **2**, two O atoms (O1 and O2) of chelated acetate and one pyridine N atom (N4) and one imine N atom (N1) of the Schiff base (L2) occupy the equatorial positions while the remaining pyridine N (N2) and imine N (N3) atoms of L2 are placed at the axial positions. The distortion of the coordination spheres is reflected in the *cisoid* [56.34(14)–112.35(13)°] and the *transoid* [148.97(13)–168.69(14)°] angles. The metal centre is displaced from the mean equatorial plane by 0.011 Å. The average values of Zn-N(L2) and Zn-O(OAc) bond distances are 2.124 Å and 2.275 Å, respectively. It is interesting to note that the Zn-O distance in chelated form is so lengthened (2.275 Å) that it does not only overcome the Zn-O bond distance [1.953(3) Å] of terminal acetate in **1** but also the bond distance (2.124 Å) of Zn-N(Schiff base). The four-membered chelate loop formed by this chelating carboxylate is a major factor for such enhancement. One four-membered chelate ring formed by the acetate and two five-membered and one seven-membered chelate rings formed by L2 surround the Zn1 centre. The tetradentate ligand is twisted around the zinc(II) centre such that the two planes containing the unsaturated chelate rings (Zn1, N3, C17, C18, N4) and (Zn1, N1,

Figure 7. Thermal behaviour of **1**.

Figure 8. Thermal behaviour of **2**.

C1, C2, N2) are inclined at 61.12° to each other. The butylenic arm of L2 is to some extent puckered.

In the crystalline state, mononuclear units in **1** are engaged in weak cooperative intermolecular O-H...O hydrogen bonds (table 4) involving O6 and H119 atoms of crystalline water molecule and free O2 atom of acetate unit. Further, C-H...F hydrogen bonds involving C14 and H14B atoms of propylenic arm and neighbouring F1 atom of hexafluorophosphate unit lead to formation of a 1D chain (figure 5) along the crystallographic *c*-axis. In compound **2** anion... π interactions between F6 atom of hexafluorophosphate and neighbouring pyridine ring and π ... π interactions involving two neighbouring pyridine rings (tables 5 and 6) give rise to a 2D sheet (figure 6) structure along the crystallographic *ab*-plane.

3.4 Thermal study

Thermogravimetric analyses of compounds **1** and **2** were carried out to examine their thermal stabilities. The crushed single crystals of **1** and **2** were heated between 40°C and 800°C temperature in the static atmosphere of dinitrogen at a heating rate of $10^\circ\text{C min}^{-1}$. The TG curve of **1** (figure 7) shows that compound **1** loses one water molecule (Obs.: 1.9%, Calc.: 2.59%) in the temperature range 106 – 241°C . The next step in weight loss is associated with the removal of the acetate moiety and the Schiff base (Obs.: 72.8%, Calc.: 66.8%) in the temperature range 241 – 792°C . On the other hand, compound **2** is devoid of water molecule and is stable up to 231°C (figure 8). The weight loss in **2** is in line with the removal of acetate group and the Schiff base (Obs.: 81.1%, Calc.: 69.45%) within the temperature range 231 – 797°C .

4. Conclusion

In the present study, two zinc(II) acetate complexes in combination with two different tetradentate Schiff bases have been isolated and X-ray crystallographically characterized. A subtle change in coordination geometry from square pyramid to octahedral in going from **1** to **2** was observed with change of the end-capping ligands. In the crystalline state, different types of non-covalent forces in the complexes promote of dimensionalities with different crystalline architectures via cooperative O-H...O and C-H...F hydrogen bonds and anion... π and π ... π interactions. The thermal behaviour shows that the frameworks in complexes **1** and **2** exhibit different stabilities. The compounds are examples of good luminous materials.

Supplementary Information

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center Nos. 1009238 (**1**) and 1009239 (**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>).

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