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Thermally stable luminescent zinc–Schiff base complexes: A thiocyanato bridged 1D coordination polymer and a supramolecular 1D polymer

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ABSTRACT

A single thiocyanato bridged 1D polymeric zinc complex with dinuclear asymmetric unit $[Zn_2L^1(\mu_{1,3}-SCN)(SCN)]_n$ (1) and a dimeric zinc complex $[Zn_2L^2(NCS)(OOCCH_3)(CH_3OH)_2]$ (2) have been synthesized using two different Schiff bases N,N'-bis(3-methoxysalicylidenimino)-1,3-diaminopropane (L^1H_2) and N,N'-bis(3-ethoxysalicylidenimino)-1,3-diaminopropane (L^2H_2) , respectively. All the ligands and the complexes have been characterized by microanalytical and spectroscopic techniques. The structures of the complexes have been conclusively determined by single crystal X-ray diffraction studies. Thermogravimetric analysis has been performed to investigate their thermal stability. Finally, the photoluminescence properties of the complexes as well as their respective ligands have been investigated with a comparative approach.

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1. Introduction

Zinc is an important transition metal in chemistry as well as in biology. It plays an important role in cellular phenomena, e.g., enzyme catalysis [1], apoptosis [2] and neurotransmission [3]. In addition, zinc is the second most abundant trace metal after iron in biological systems and essential to all forms of life [4-7]. Its d¹⁰ configuration permits a wide range of symmetries and various coordination numbers, i.e., 4, 5 or 6, with suitable geometries (tetrahedral, square pyramidal/TBP and octahedral) which is very important criterion for designing a wide variety of metal-organic frameworks. Moreover, luminescent compounds are attracting current research interest because of their vast applications in emitting materials for organic light emitting diodes, light harvesting materials for photocatalysis and fluorescent sensors for organic or inorganic analysts [8]. Hence it is important to understand the coordination chemistry and luminescence between Group 12 metal ions for developing new fluorescent sensors materials [8]. In 1987 Tang and VanSlyke [9] reported Al(q)₃ (q: 8-hydroxyquinolinyl) as the first bilayer organic light-emitting diode (OLED). Since then, numerous attempts have been made in order to design green, blue, and red luminescent complexes to develop full color RGB devices as those three fundamental colors can be mixed to produce the whole visible spectrum. Interestingly, there is an analogy between the emission behavior of salicylaldehyde Schiff bases and 8-hydroxyquinoline since both the ligands have similar chromophoric groups i.e., a hydroxy group, a coordinating imine N atom and a delocalized π system [10]. Therefore, zinc(II) complexes of salen type Schiff bases are expected to show good luminescence properties and the introduction of electron-donating groups into the salicylidene moiety of Zn(II) complexes enhances the quantum yield of photoluminescence [11]. Our research group has already reported some luminescent complexes of different salicylaldimino Schiff bases with zinc [12–15] as well as lanthanoids [16]. In continuation of our earlier work, we have synthesized two N2O4 donor compartmental Schiff bases LH₂ by the condensation of one equivalent of 1,3-diamines and two equivalent of 3-alkoxysalicylaldehyde derivatives: N, N'-bis(3-methoxysalicylidenimino)-1,3-diaminopropane (L^1H_2) and N,N'-bis(3-ethoxysalicylidenimino)-1,3-diaminopropane (L^2H_2) (Scheme 1). Zinc complexes of these ligands have been synthesized in presence of NaSCN for the both cases to obtain compounds of the following formulation $[Zn_2L^1(\mu_{1,3}$ -SCN)(SCN)]_n (1) and $[Zn_2L^2(NCS)(OOCCH_3)]$ $(CH_3OH)_2$] (2).

The pseudohalide ion, SCN⁻ has coordinated the metal ions in both terminal and bridging modes. While bridging the adjacent metal centers thiocyanate furnishes various coordination modes

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Scheme 1. The synthetic routes and the mode of coordination of the Schiff base ligands.

as depicted in Scheme 2(A–E). In different bi and polynuclear complexes these bridging modes have been identified as $\mu_{1,1}$ -NCS (A) [17], $\mu_{1,1}$ -SCN (B) [18], $\mu_{1,3}$ -NCS (C) [19], $\mu_{1,1,3}$ -SCN (D) [20] and $\mu_{1,1,1,3}$ -SCN (E) [21]. The first three modes of bridging usually form dinuclear complexes [17,22,23]. $\mu_{1,1,3}$ -SCN, $\mu_{1,1,1,3}$ -SCN and also $\mu_{1,3}$ -NCS modes are prone to form polynuclear 2D networks with double SCN⁻ bridging in presence of bidentate ligands [24–26] and 1D chain structures with single or double SCN⁻ bridging in presence of tri or tetradentate ligands [27,28]. The complexes reported herein contain pendant SCN⁻ ligands. Moreover $\mu_{1,3}$ -bridging in SCN⁻ has lead to a single chain 1D polymer.

In this paper, we have reported the synthetic details, spectral characterizations, thermal investigations, along with X-ray crystal structures and photophysical studies of **1** and **2** where thiocyanate acts as terminal ligand as well as end-to-end bridging in presence of a potentially hexadentate Schiff base.

2. Experimental

2.1. Materials

All chemicals and solvents employed for the syntheses were of analytical grade and used as received without further purification. *O*-vanillin (i.e. 2-hydroxy-3-methoxybendaldehyde),



Scheme 2. Different coordination modes of thiocyanate ligand.

2-hydroxy-3-ethoxybenzaldehyde, 1,3-propylenediamine (i.e. 1,3diaminopropane) and sodium thiocyanate were purchased from Aldrich Chemical Company. Zinc acetate dihydrate was purchased from E. Merck, India.

2.2. Physical measurements

The Fourier Transform Infrared spectra were recorded in the range 4000–400 cm⁻¹ on a Perkin-Elmer RX I FT-IR spectrophotometer with solid KBr pellets. C. H. and N microanalyses were carried out with a Perkin-Elmer 2400 II elemental analyzer. ¹H NMR spectra of the Schiff base ligands and that of complex 2 were recorded on a Bruker 300 MHz FT-NMR spectrometer using trimethylsilane as internal standard in CDCl₃ solvent. UV-Vis absorption spectra were recorded on a Specord 205 (Analytik Jena) spectrometer. Steady state emission and excitation spectra were recorded on a Horiba Jobin Yvon Fluorolog 3 spectrometer working with a continuous 450W Xe lamp. For the measurement in the solid state, the spectrometer was fitted with a Quanta- Φ integrating sphere from Horiba. Detection was performed with a Hamamatsu R928 photomultiplier. All spectra were corrected for the instrumental functions. When necessary, a 370 nm cutoff filter was used to eliminate the second order artifacts. The ligand emission lifetime in EtOH solution was measured in time-resolved mode, by monitoring the decay at the maximum of the emission spectrum using a Jobin Yvon FluoroHub single photon counting controller, fitted with a 303 nm Jobin Yvon NanoLED. The decays were analyzed with DataStation v2.4. The same set up was used for solid state lifetime measurements using 2 mm inner diameter quartz tube and the front face configuration of the instrument. Luminescence quantum yields in solution were measured according to conventional procedures, with diluted solutions (optical density <0.05), using Rhodamine 6G in methanol ($\Phi = 0.86$) as Ref. [29]. Estimated errors are +15%.

Solid state studies and quantum yields were determined using a Hamamatsu Quantaurus-QY integrating sphere according to the procedure described in Ref. [30a,b]. The luminescence quantum yield Φ is given by:



Scheme 3. Proton numbering scheme of Schiff base ligands.

Table 1

Crystal structure parameters of the complexes 1 and 2.

Parameters	1	2
Empirical formula	$C_{21}H_{20}N_4O_4S_2Zn_2$	C26H35N3O8SZn2
Formula weight	587.31	680.37
T (K)	150	100(2)
Crystal system	orthorhombic	orthorhombic
Space group	Pbca	P2(1)2(1)2(1)
a (Å)	11.5131(4)	7.8386(9)
b (Å)	18.4518(7)	16.2279(17)
<i>c</i> (Å)	22.0191(7)	23.188(2)
$V(Å^3)$	4677.7(3)	2949.7(6)
Ζ	8	4
D_{calc} (Mg m ⁻³)	1.668	1.532
μ (mm ⁻¹)	2.265	1.748
F (000)	2384	1408
θ Range (°)	1.850-27.860	2.51-27.59
Total data	11002	71919
Unique data	5561	6782
Observation data $[I > 2\sigma(I)]$	3395	6355
$R_1[I > 2\sigma(I)]$	0.0394	0.0225
$wR_2[I > 2\sigma(I)]$	0.0418	0.0523
Goodness of fit (GOF) on F^2	1.1101	1.013
R _{int}	0.039	0.064
Residuals (e Å ⁻³)	0.54, -0.46	0.30, -0.41

$$\Phi = \frac{E_i \lambda - (1 - A) E_0 \lambda}{L_e(\lambda) A} \tag{1}$$

Where

$$A = \frac{L_0(\lambda) - L_i(\lambda)}{L_0(\lambda)} \tag{2}$$

in which $E_i(\lambda)$ is the integrated luminescence of the film caused by direct excitation, $E_0(\lambda)$ is the integrated luminescence of the film caused by illumination from the sphere, A is the absorbance of the film, $L_e(\lambda)$ is the integrated excitation profile from the empty integration sphere (without the sample), $L_0(\lambda)$ is the integrated excitation profile when the sample is diffusively illuminated by the integration sphere and $L_i(\lambda)$ is the integrated excitation profile upon direct excitation of the sample by the incident beam. The integrated spectra were corrected for the wavelength sensitivity of the photomultiplier and the spectral response of the sphere using correction functions furnished by the supplier.

Table 2

IR spectral data (cm⁻¹) of ligands L^1H_2 and L^2H_2 and complexes 1 and 2.



Fig. 1. ¹H NMR spectra of L¹H₂, L²H₂ and Complex 2 in CDCl₃ solvent.

Luminescence quantum yields in solutions were determined on optically diluted samples (optical density <0.05) according to Eq. (3) [30c]:

$$\Phi_{\rm x} = \Phi_{\rm ref} \times \left(\frac{n_{\rm x}^2}{n_{\rm ref}^2}\right) \times \left(\frac{\int I_{emx}(\lambda)d(\lambda)}{\int I_{emref}(\lambda)d(\lambda)}\right) \times \left(\frac{o.d._{\rm ref}}{o.d._{\rm x}}\right) \tag{3}$$

in which the subscripts *x* and *ref* refer respectively to the sample and the reference, *n* is the refractive index of the solution, $I_{em}(\lambda)$ is the emitted intensity at wavelength λ , and *o.d.* is the optical density of the sample.

2.3. Syntheses

2.3.1. Synthesis of the Schiff base ligands

Both the ligands were synthesized in similar ways as previously reported [31]. L^1H_2 is the 1:2 condensation product of

		-				
Compound	v(C=N)	$v(C-O_{Phenolic})$	v(0-H/H ₂ O)	v(Zn–N)	$v(SCN^{-})$	v(COO ⁻)
L^1H_2	1641	1254	3449	-	_	-
L^2H_2	1640	1260	3448	-	-	-
1	1622	1226	-	454	2127-2109	-
2	1627	1224	3432	439	2086	1564-1413

1,3-diaminopropane with 3-methoxy-2-hydroxybenzaldehyde, and L^2H_2 is the 1:2 condensation product of 1,3-diaminopropane with 3-ethoxy-2-hydroxybenzaldehyde. ¹H NMR for L^1H_2 (δ , 300 MHz): 2.11(t, J = 6.45, 2H⁸), 3.74 (t, J = 8.1, 2H⁷), 3.91 (s, 3H¹), 6.79–6.95 (m, 1H², 1H³, 1H⁴), 8.37 (s, 1H⁵), 13.94 (s, 1H⁶), ppm; ¹H NMR for L^2H_2 (δ , 300 MHz): 1.27 (t, J = 6.98, 3H¹), 2.09 (t, J = 6.7, 2H⁹), 3.73 (t, J = 6.5, 2H⁸), 4.12 (q, 2H²), 6.76–6.94 (m, 1H³, 1H⁴, 1H⁵), 8.37 (s, 1H⁶), 13.94 (s, 1H⁷), ppm (Scheme 3 and Fig. 1).

2.3.2. Synthesis of the complexes

2.3.2.1. $[Zn_2L^1(\mu_{1,3}$ -SCN)SCN]_n (1). Zinc acetate dihydrate (0.439 g, 2 mmol) was dissolved in 10 mL methanol. A methanolic solution of the Schiff base (L¹H₂) (0.342 g, 1 mmol) was added to it followed by drop wise addition of aqueous solution of NaSCN (0.162 g, 2 mmol). The mixture was allowed to stir for 40 min with gentle heating. The bright yellow solution was filtered and kept in refrigerator for crystallization by slow evaporation. After 2 days colorless plate shaped single crystals suitable for X-ray crystallography were obtained, yield 0.440 g (75%). Anal. Calc. for C₂₁H₂₀N₄O₄Zn₂S₂ (587.31): C, 42.91; H, 3.41; N, 9.53. Found: C, 42.95; H, 3.53; N, 9.43%. FT-IR (KBr, cm⁻¹): v(C=N) 1622, v(C-O_{Phenolic}) 1226, v(Zn-N) 454.

2.3.2.2. $[Zn_2L^2(NCS)(OOCCH_3)(CH_3OH)_2]$ (2). Compound 2 was prepared in a similar fashion as in case of 1, using 1 mmol of L^2H_2 (0.370 g) in methanol as Schiff base ligand. Yellow needle shaped single crystals suitable for X-ray diffraction were obtained after three days. Crystals were isolated by filtration and were air dried, yield 0.537 g (79%). *Anal.* Calc. for C₂₆H₃₅N₃O₈SZn₂ (680.37): C, 45.86; H, 5.14; N, 6.17. Found: C, 45.77; H, 5.21; N, 6.15%. FT-IR (KBr, cm⁻¹): v(C=N) 1627, $v(C-O_{Phenolic})$ 1224, v(O-H) 3432, $v_{asym}(COO^-)$ 1564, $v_{sym}(COO^-)$ 1413, v(Zn-N) 439. ¹H NMR (δ , 300 MHz): 1.33 (t, J = 6.98, 3H¹), 2.01 (s, 3H of CH₃COO⁻), 2.22 (t, J = 6.7, 2H⁹), 3.48 (s, 3H of CH₃OH), 3.90 (t, J = 6.5, 2H⁸), 4.22 (q, 2H²), 5.29 (s, OH of CH₃OH), 6.65–6.91 (m, 1H³, 1H⁴, 1H⁵), 8.13 (s, 1H⁶), ppm (Scheme 3 and Fig. 1).

2.4. Crystallographic data collection and structure refinements

Intensity data were collected using Mo K α radiation ($\lambda = 0.71069$ Å) with a Nonius Kappa CCD diffractometer at 150 K for **1** and on a Bruker X8 Apex2 diffractometer at 100 K for **2**. Structures were solved by direct methods using the sIR97 [32] program for **1** and by SHELXS 97 program [33] for **2**. Structures were refined by full-matrix least-squares methods with the program CRYSTALS [34] for **1** and SHELXL 97 [33] for **2**. In complex **2**, one of the CH₃ moieties of the two ethoxy substituents is disordered over two positions with 60.0(5)% occupancy for the major component (C25A). Selected crystallographic data, experimental conditions and relevant features of the structural refinements for all the complexes are summarized in Table 1.

3. Results and discussion

3.1. Fourier transform infrared spectra

Fourier transform infrared spectra of both complexes were analyzed and compared with those of the corresponding ligands L^1H_2 and L^2H_2 and the stretching vibrations are listed in Table 2. Strong sharp absorption bands at 1641 and 1640 cm⁻¹ in the spectra of L^1H_2 and L^2H_2 , respectively, due to the C=N stretching indicate the formation of the desired Schiff base ligands. Condensation of all the primary amine groups have been confirmed by the absence of the N–H stretching bands in the region 3150–3450 cm⁻¹. In the complexes, the $v_{C=N}$ stretching vibrations at 1622 and 1627 cm⁻¹ in **1**

and 2, respectively, have been shifted considerably towards lower frequencies compared to that of the free ligands indicating the coordination of the imine nitrogen atom to the metal center [35]. Well defined bands observed at 3449 and 3448 cm^{-1} in the spectra of $L^1\text{H}_2$ and L²H₂, respectively, are due to O-H stretching, which disappeared in the spectra of 1 upon deprotonation of the O-H group during complexation; while a band at 3432 cm^{-1} in the spectrum of **2** may be attributed to the presence of coordinated methanol molecules. The phenolic C–O stretching bands at 1254 and 1260 cm⁻¹ in the spectra of $L^{1}H_{2}$ and $L^{2}H_{2}$, respectively were shifted to 1226 and 1224 cm⁻¹ in case of 1 and 2, respectively, supporting the deprotonation and coordination of the phenolic oxygen donors to the metal centre. The ligand coordination to the metal centre were indicated by a band appearing at 454 cm^{-1} for **1** and at 439 cm^{-1} for **2**, which were mainly assigned to $v_{(Zn-N)}$ in each case. Both complexes show characteristic sharp v_{SCN} bands at 2127–2109 cm⁻¹ in **1** and at 2086 cm⁻¹ in 2, respectively. In 1 the v_{SCN} band is bifurcated indicating two different coordination modes of the SCN⁻ ligand. In 2, acetate ligands display asymmetric and symmetric stretching vibrations at 1564 and 1413 cm⁻¹, respectively. Thus the characteristic vibrational bands of the above mentioned groups in complexes 1 and 2 give a superficial idea about their structures which are very much consistent to their crystal structures.

3.2. ¹H NMR spectroscopy

¹H NMR spectroscopy has been used to extract information regarding the formation of the Schiff base ligands $(L^1H_2 \text{ and } L^2H_2)$ and mode of coordination of the ligand L²H₂ with the Zn^{II} centers in complex 2. We could not obtain NMR spectrum of complex 1 due to its insolubility and possibility of rupture of polymeric structure in conventional solvents. The NMR proton numbering scheme of the ligands are represented in Scheme 3 and the corresponding spectra of the ligands and complex **2** are represented in Fig. 1. In the NMR spectra of the free ligands no broad peak was observed in the region δ 5.0 to δ 8.0 ppm, indicating the absence of free – NH₂ functionality, supporting the formation of the ligands [36]. The broad peak at $\delta \approx 13.94$ ppm stands for the phenolic OH⁶ and OH^7 of the ligands L^1H_2 and L^2H_2 , respectively. The peaks in between δ = 6.76 and 6.95 ppm correspond to the aromatic protons of the ligands. The protons H⁵ and H⁶ attached to the imino carbon of $L^{1}H_{2}$ and $L^{2}H_{2}$, respectively are strongly downfield shifted $(\delta \approx 8.37 \text{ ppm})$ due to the influence of both phenolic –OH and imino N groups in its close vicinity. The methylene protons (H^7 for L^1H_2) and H^8 for L^2H_2) being very close to the imino nitrogen, are deshielded and appear as a 2H triplet at $\delta \approx 3.7$ ppm. The three methyl hydrogens (H^1) attached to the aromatic oxygen of L^1H_2 appear as a 3H singlet at $\delta \approx 3.91$ ppm but for L²H₂ these hydrogens are intervened by a -CH₂ group and appear at upper field as a triplet at $\delta \approx 1.27$ ppm. Additionally, spectrum of L²H₂ contains a quartet at $\delta \approx 4.12$ ppm due to the intervening $-CH_2$ group protons (H²) which are in the paramagnetic influence of the aromatic oxygen.

The complex **2** was also characterized by proton NMR (Fig. 1) where it resembles that of the corresponding ligand except the fact that signal of the phenolic OH proton which gets deprotonated during complextation is missing. Moreover, it is clearly observed that the signals of H³–H⁶ are broadened compared to the free ligand (L²H₂) possibly due to spin–lattice relaxation caused by paramagnetic impurities in the complex [37]. ¹H NMR spectrum of **2** contains three additional singlet at $\delta \approx 2.01$, 3.48 and 5.29 ppm, respectively. $\delta \approx 2.01$ ppm can be assigned to the three protons of the coordinated CH₃COO⁻ group, $\delta \approx 3.48$ and 5.29 ppm are due to the three methyl proton and hydroxyl proton respectively, of the coordinated CH₃OH. The results obtained from the NMR spectra are in agreement with the structure obtained by the X-ray analysis.

3.3. Crystal structure descriptions

3.3.1. $[Zn_2L^1(\mu_{1,3}-SCN)(SCN)]_n$ (1)

The X-ray structural analysis reveals that complex **1** has a zigzag polymer chain structure. A perspective view of the dimeric asymmetric unit of **1** is presented in Fig. 2 and the bond distances and angles around the metal centers are listed in Table 3. The asymmetric unit of **1** contains a penta coordinated and a hexacoordinated Zn ions (Zn1 and Zn2, respectively) connected by doubly bridging phenoxo oxygens (O9 and O23) of a hexadentate Schiff base ligand. There are three thiocyanate ligands, one pendant from Zn2, and the other two bridge two adjacent molecular units forming an undulating infinite chain. The Zn1^{···}Zn2 separation (3.203 Å) is within the range of previously reported complexes [38,39].

Zn1 is penta coordinated with a distorted square pyramidal geometry with Addison parameter. $\tau = 0.022$ ($\tau = |\beta - \alpha|/60^\circ$ where β and α are the two largest angles around the central atom. $\tau = 0$ for a perfect square pyramidal and **1** for a perfect trigonal bipyramidal geometry) [40]. The N₂O₂ chromophore of $(L^{1})^{2-}$ forms the basal plane and the apical position is occupied by S31 end of a bridging thiocyanate ligand. Zn1 is displaced by 0.410 Å towards the apical S31 atom from the mean square plane passing through N11, N15, O9 and O23. The second metal centre, Zn2 is tetrahedral with $\tau_4 = 0.947$ (τ_4 is the geometry index for four-coordinated complexes and is defined as $\tau_4 = {360^\circ - (\alpha + \beta)}/{141^\circ}$, where α and β – the two largest θ angles in the four-coordinate species) [41]. Zn2 is connected through the phenoxo O atoms of $(L^{1})^{2-}$ (O9 and O23; average Zn–O 2.022 Å) and two thiocyanate N atoms, N43 of a pendant SCN⁻ and N33 of a μ -bridging SCN⁻ ligands. There are two additional much longer (average 2.545 Å) connections to the methoxo O atoms (O2 and O24) of $(L^1)^{2-}$.

The Zn1 atom of each asymmetric unit is connected to the Zn2 atom of an adjacent molecule by the basal–apical coordination mode of $\mu_{1,3}$ -SCN⁻ ligand. Thus a single thiocyanato bridged undulating molecular chain develops along the crystallographic *a* axis (Fig. 3).

3.3.2. $[Zn_2L^2(NCS)(OOCCH_3)(CH_3OH)_2]$ (2)

Fig. 4 represents a perspective view of the asymmetric unit of complex **2** with the atom labeling scheme. Selected bond lengths



Fig. 2. Perspective view of the asymmetric unit of complex 1, H-atoms have been removed for clarity.

Table 3	
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Selected bond distances (Å) and bond angles (°) in 1 and 2.

1		2	
Bond distance (Å)			
Zn1-N11	2.044(3)	Zn1-N10	2.0328(16)
Zn1-N15	2.037(3)	Zn1-N14	2.0616(17)
Zn1-09	2.044(3)	Zn1-08	2.0576(13)
Zn1-023	2.040(3)	Zn1-022	2.0317(14)
Zn1-S31	2.465(12)	Zn1-033	2.1512(15)
Zn2-N33	1.983(4)	Zn1-035	2.3198(15)
Zn2-N43	1.953(4)	Zn2-01	2.6500(14)
Zn2-02	2.610(3)	Zn2-08	2.0324(13)
Zn2-09	2.017(3)	Zn2-022	2.0200(13)
Zn2-023	2.027(3)	Zn2-023	2.5153(16)
Zn2-024	2.481(3)	Zn2-029	1.9456(14)
		Zn2-N1	1.9523(18)
Bond angles (°)			
N11-Zn1-N15	97.46(14)	N10-Zn1-N14	100.74(6)
N11-Zn1-09	89.67(12)	O35-Zn1-N10	90.43(6)
N11-Zn1-O23	148.34(13)	033-Zn1-N10	90.26(6)
N11-Zn1-S31	101.87(10)	022-Zn1-N10	167.07(6)
N15-Zn1-09	159.46(12)	08-Zn1-N10	90.35(6)
N15-Zn1-023	88.97(12)	08-Zn1-N14	168.33(6)
N15-Zn1-S31	105.04(9)	022-Zn1-N14	90.43(6)
09-Zn1-023	75.28(11)	033-Zn1-N14	91.25(6)
09–Zn1–S31	92.19(8)	035–Zn1–N14	88.24(6)
023-Zn1-S31	106.31(8)	08-Zn1-022	78.16(5)
N33-Zn2-N43	124.06(15)	08-Zn1-033	92.36(6)
N33-Zn2-O2	77.33(13)	08–Zn1–O35	88.03(5)
09-Zn2-N33	113.18(13)	022–Zn1–O33	96.07(6)
N33-Zn2-023	111.69(13)	022-Zn1-035	83.34(5)
N33-Zn2-024	80.41(13)	033-Zn1-035	179.21(5)
N43-Zn2-02	86.85(13)	01-Zn2-08	66.53(5)
N43-Zn2-09	108.41(13)	01-Zn2-022	145.50(5)
N43-Zn2-023	113.32(13)	01-Zn2-023	145.61(5)
N43-Zn2-024	85.74(13)	01-Zn2-029	74.89(5)
02 - 2n2 - 09	66.69(11)	01-Zn2-N1	83.98(6)
02-2112-023	141.95(11)	08-202-022	/9.01(5)
02-2112-024	146.98(11)	08-2112-023	147.32(5)
09-2112-023	70.10(11)	08-ZIIZ-029	109.95(6)
09-2112-024	145.72(11)	08-ZIIZ-INI 022 7=2 022	111.04(0)
023-2112-024	09.57(11)	022 - 2112 - 023	120 86(E)
		022 - 2112 - 029	120.80(0)
		022-2112-191 022 7p2 020	100.33(7) 92.04(E)
		023 - 2112 - 029 023 - 7n2 - N1	84 57(6)
		O20 - ZHZ - INI	04.37(0) 110.79(7)
		029-2112-111	119.70(7)

and angles are summarized in Table 3. Complex 2 is a dinuclear cluster with a very similar Zn-ligand chelate arrangement to complex 1. However the geometry of Zn1 differs in both complexes. In 1 it is square pyramidal but it is octahedral in complex 2. The four equatorial sites are occupied by two imine nitrogen (N10, N14) and two phenoxo oxygen (08, 022) atoms of $(L^2)^{2-}$. Two methanol molecules are coordinated to Zn1 at trans-axial positions. Zn1 is displaced by 0.082 Å from the equatorial plane towards the apical oxygen atom O33. The twelve *cis*-angles $[78.16(5)^{\circ}-100.74(6)^{\circ}]$ show significant deviations from ideal octahedral bond angles and the three *trans*-angles $[167.07(6)^{\circ}-179.21(5)^{\circ}]$ less so. The average equatorial bond distances (2.0459 Å) are smaller than the average axial bond distances (2.2355 Å) (Table 3); these features indicate a *z-out* type Jahn-Teller distortion from the ideal octahedral geometry. The axial Zn-O lengths are quite different with the longer Zn–O distance 2.3198(15) cf. 2.1512(15) Å belonging to the methanol ligand which is involved with intra and intermolecular hydrogen bonding.

The second metal center (Zn2) has distorted tetrahedral geometry ($\tau_4 = 0.846$) [41] very similar to that in complex **1**. The tetrahedron around Zn2 is formed by the bridging phenoxo oxygens (O8, O22) of the Schiff base ligand, the N1 end of a terminal thiocyanate ligand and a monodentate (η^1) CH₃COO⁻ anion. Again there are two longer contacts to the ethoxo oxygens (O1, O23) of (L²)²⁻



Fig. 3. View of the polymeric arrangement in 1 running along axis *a*, H-atoms have been removed for clarity.



Fig. 4. Perspective view of the asymmetric unit of complex 2, H-atoms have been removed for clarity.

(Table 3). A similar feature of longer methoxy contacts compared to phenoxy is also seen in an alike trizinc methoxy phenoxy Schiff base complex [42].

The dinuclear units of **2** are connected by bifurcated $OH \cdots O$ hydrogen bonds which form a chain along the crystallographic *a* axis. The hydrogen atom (H33) belonging to the methanol molecule coordinated to a zinc metal ion (Zn1) of one dimer forms intermolecular hydrogen bond with the non-coordinated oxygen atom (O32) of the carboxylate group coordinated to a zinc metal ion (Zn2) of a neighboring dimer. This oxygen atom (O32) is also involved in an intra-hydrogen bond with the hydrogen atom (H35) belonging to a second methanol molecule, positioned on the same side and coordinated to the second zinc ion (Zn1) (Fig. 5, Table 4).

3.4. Photoluminescence studies

3.4.1. Absorption and emission of the ligands in EtOH

The UV–Vis absorption spectra of the Schiff-base ligands L^1H_2 and L^2H_2 were recorded at room temperature in EtOH solutions (Fig. 6). The two spectra exhibit three distinct absorption bands centered at 264 nm (ε = 13300 M⁻¹ cm⁻¹ for L^1H_2 and 12050 M⁻¹ - cm⁻¹ for L^2H_2), 330 nm (ε = 2780 M⁻¹ cm⁻¹ for L^1H_2 and 2660 M⁻¹ cm⁻¹ for L^2H_2) and 421 nm (ε = 1360 M⁻¹ cm⁻¹ for L^1H_2 and 1050 M⁻¹cm⁻¹ for L^2H_2). They can be assigned to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions of the Schiff-base ligands. A similar absorption spectrum had been previously recorded for the *N*,*N*/bis(salicylidene)-1,3-diaminopentane L^0H_2 [13], but the substitution of the phenol rings by methoxy groups in L^1H_2 , or ethoxy groups in L^2H_2 , resulted in a 20 nm bathochromic shift of all the absorption bands. Finally, a shoulder is also observed at *ca*. 295 nm with ε = 4290 M⁻¹ cm⁻¹ for L^1H_2 and 3570 M⁻¹ cm⁻¹ for L^2H_2 .

Upon excitation into the UV domain at 274 nm, the two ligands gave rise to broad fluorescence spectra with maxima pointing both at 474 nm. The corresponding excitation spectra are dominated by two intense bands at 274 and 350 nm (Fig. 7). Interestingly, the strong excitation bands centred at *ca.* 350 nm do not correspond to any of the transitions recorded in the absorption spectra. This behaviour is typical of salen-based compound and has been correlated to the presence of an equilibrium between the ketoamine and the enolimine tautomers due to the formation of strong N···H bonds between the imino-phenolate moiety [43].

The emission spectra of L^1H_2 and L^2H_2 are presented in Fig. 8. Interestingly, the emission maxima are bathochromically shifted by 30 nm, in comparison with the ligand L^0H_2 , as a result of the incorporation of the electron donating methoxy or ethoxy group on the salen skeleton. Similar absorption and emission maxima have been previously reported for a tridentate Schiff base ligand with a methoxy group in ortho position of the phenol moiety [44]. The corresponding quantum yields have been determined in EtOH with the high dilution method relative to rhodamine 6G ($\Phi = 0.86$) [29]. The measured quantum yields amount to 8.9×10^{-3} and 4.6×10^{-3} for L^1H_2 and L^2H_2 , respectively and they



Fig. 5. Hydrogen bonded chain propagated along the crystallographic *a* axis.

Table 4					
Hvdrogen	bond	dimensions	for	complex 2.	

D−H···A	d(D–H) Å	d(H···A) Å	$d(D{\cdots}A) \; \mathring{A}$	<(DHA)°
033–H33…032#1	0.860(16)	1.826(18)	2.659(2)	163(3)
035–H35…032	0.873(18)	1.82(2)	2.667(2)	163(3)

Symmetry transformations used to generate equivalent atoms: #1: x - 1, y, z.



Fig. 6. UV–Vis absorption spectra of L^1H_2 (red) and L^2H_2 (blue) (C_{ligand} = 2 \times 10 $^{-4}$ M in EtOH). (Colour online.)

are similar to the value previously obtained for the ligand *N*,*N*^{/-} bis(salicylidene)-1,3-diaminopentane L^0H_2 (9.3 × 10⁻³ in MeOH) [13]. From these results, one can notice that L^1H_2 is more emissive than L^2H_2 , which is probably due to the replacement of the methyl groups by ethyl groups, the later bringing additional vibrational quenching from the C–H bonds of the alkyl chains. The luminescent decays have been measured by Time Correlated Single Photon Counting (*TCSPC*) Lifetime Spectroscopy with a NanoLED emitting at 303 nm. The decay curves can only be conveniently fitted with bi-exponential models, with lifetimes in the nanosecond range (Table 5). These bi-exponential fluorescence decay profiles may be related to the presence of two species in solution, as for instance the ketoamine and the enolimine isomers.



Fig. 7. Excitation spectra of the ligands L^1H_2 (red, $\lambda_{em} = 474$ nm) and L^2H_2 (blue, $\lambda_{em} = 478$ nm) in EtOH, normalized on the maximum of the low energy excitation band. (Colour online.)

3.4.2. Luminescence properties of the complexes

The photophysical properties of the complexes were examined in the solid state. Selected data are summarized in Table 6. Upon excitation of the ligand at ca. 350 nm, the two complexes display broad emission spectra with maxima at 497 and 512 nm for 1 and 2, respectively (Fig. 9). The overall emission spectra are bathochromically shifted in comparison to the free ligands. Although very weak, these luminescence emission spectra are typical for salen-type Schiff-base Zn(II) complexes and can be assigned to intraligand $\pi \rightarrow \pi^*$ transitions [45,46]. A similar emission pattern had been previously recorded for the polymeric Zn(II) complex with ligand L⁰H₂. However, the introduction of methoxy or ethoxy substituents in the ortho positions of the phenol rings is responsible for a 60 nm red shift of the emission maxima, as recorded for the free ligands. The corresponding excitation spectra are presented in Fig. 10 and show a strong excitation from the UV region to 420 nm, as observed in the case of the free ligands. However, saturation phenomena in the solid state prevented an accurate determination of the maxima of excitation.

The luminescence quantum yields and lifetimes of the Zn(II) complexes have been checked in the solid state (Table 6). 1 and



Fig. 8. Emission spectra of L^1H_2 (red, λ_{exc} = 342 nm) and L^2H_2 (blue, λ_{exc} = 358 nm) in EtOH normalized according to their luminescence quantum yields. (Colour online.)

Table 5											
Photophysical	properties	of	L^1H_2	and	L^2H_2	in	absolute	EtOH	solution	at	room
temperature.											

Ligand	Absorption λ_{ab}/nm (log[ϵ/M^{-1} cm ⁻¹])	Excitation λ _{max} /nm	Emission $\lambda_{max}/nm(\Phi)$	Lifetime τ_i/ns ($A_i /\%$) [$i = 1,2$]
L^1H_2	264 (4.12), 330 (3.44), 421 (3.13)	342	$\begin{array}{c} 474 \\ (8.9 \times 10^{-3}) \end{array}$	$\tau_1 = 3.0 \text{ ns} (71)$ $\tau_2 = 5.6 \text{ ns} (29)$
L ² H ₂	264 (4.08), 330 (3.42), 421 (3.02)	359	$\begin{array}{l} 478 \\ (4.6 \times 10^{-3}) \end{array}$	$\tau_1 = 1.7 \text{ ns} (39)$ $\tau_2 = 5.4 \text{ ns} (61)$

 Table 6

 Photophysical properties of the polymeric complexes 1 and 2 in the solid state.

Complex	Excitation λ _{ex} /nm	Emission λ _{em} /nm	Lifetime $\tau_i/\text{ns} (A_i /\%) [i = 1,2]$
1	342	497	$\tau_1 = 2.3 \text{ ns} (58)$
2	359	512	$\tau_2 = 4.1 \text{ ns} (42)$ $\tau_1 = 2.8 \text{ ns} (43)$ $\tau_2 = 6.4 \text{ ns} (57)$

2 give rise to very weak emission bands and their quantum yields are too low to be determined accurately (<1%). In contrast to other highly luminescent Zn(salen) complexes [14], the weak luminescent of **1** and **2** may be attributed to additional non-radiative deactivation pathways, possibly through electron transfer phenomenon resulting from the presence of isothiocyanate anions, as previously observed for other coordination compounds [47,48]. Bi-exponential luminescence decays have been recorded and the corresponding lifetimes are presented in Table 6. For each polymer, a short component with a lifetime of *ca*. 2 ns has been measured, in agreement with the lifetime reported for monometallic Schiff base Zn(II) complexes (1.41–2.52 ns) [45,46]. In that case, a longer component with a lifetime around 5–6 ns is also observed, in agreement with the values measured for the free ligands.

The photophysical properties of complex **2** were also examined in DMSO solutions (Fig. 11). The UV–Vis absorption spectra is bathochromically shifted in comparison to the one of the free ligands and exhibits two main bands centered at 279 nm ($\varepsilon = 22460 \text{ M}^{-1} \text{ cm}^{-1}$) and 370 nm ($\varepsilon = 12050 \text{ M}^{-1} \text{ cm}^{-1}$). Upon excitation into the transitions of the Schiff-base ligand at 370 nm, a broad fluorescence is observed with a maximum at



Fig. 9. Normalized emission spectra of **1** (red, λ_{exc} = 342 nm) and **2** (blue, λ_{exc} = 358 nm) in the solid state. (Colour online.)



Fig. 10. Normalized excitation spectra of **1** (red, $\lambda_{em} = 497 \text{ nm}$) and **2** (blue, $\lambda_{exc} = 512 \text{ nm}$) in the solid state. (Colour online.)

494 nm, close to the maximum observed in the solid state, which indicated that the complex is stable in solution and also that complexation drives the equilibrium between the ketoamine and enolimine tautomers observed for the free ligand, towards the enolimine isomer as single species. The corresponding excitation spectrum is characterized by an intense band centered at 370 nm, which is in good agreement with the absorption spectrum (Fig. 11).

However, the complex is not much stronger emissive in solution than in the solid state and a luminescence quantum yield below 1% has been measured. Time decay profiles have also been recorded and satisfactorily fitted to bi-exponential decays with lifetimes of the same order of magnitude than the one measured for the free ligand in EtOH solution ($\tau_1 = 0.58$ ns, 67%; $\tau_2 = 9.48$ ns, 33%).

3.5. Thermogravimetric analysis

The study of the thermal stability of the complexes is very important in order to use them as emissive materials. The thermal stability of the complexes **1** and **2** have been investigated using



Fig. 11. UV–Vis absorption spectrum of 2 (purple) in DMSO and corresponding excitation (red, λ_{em} = 494 nm) and emission spectra (blue, λ_{ex} = 370 nm). (Colour online.)

TGA over a temperature range 25–600 °C in a single run in a dynamic nitrogen atmosphere.

Thermogravimetric studies of **1** and **2** indicate that the complexes are stable up to 354 and 510 °C, respectively. For **1** the first stage of mass loss occur in the temperature range 354–375 °C with a total mass loss of ~19.03% (calcd. 19.75%) per formula unit, respectively which corresponds to the loss of one terminal and one bridging thiocyanate moiety. No further mass loss was observed after the above mentioned temperatures. For **2**, the first stage of weight loss ~9.18% (calcd. 9.41%) occurs in the temperature range 120–150 °C which corresponds to the loss of the two coordinated methanol molecules. On further heating the species decomposes in the range 520–535 °C corresponding to the elimination of the one terminal thiocyanate ligand with a further mass loss of ~8.50% (calcd. 8.52%).

4. Conclusion

This paper describes the synthesis and structural aspects of two zinc complexes with the potentially hexadentate N₂O₄ donor Schiff base ligands and thiocyanate coligands. The X-ray diffraction study reveals that both the Zn^{II} complexes have dinuclear core chelated by the compartmental Schiff bases. Complex 1 develops a 1D zig-zag molecular chain through the end-to-end bridging thiocyanate ligand whereas thiocyanate is non-bridging in complex 2 possibly because of more steric hindrance caused by the ethyl side chain of the Schiff base that prevents further association of the dinuclear units. Although, an intermolecular hydrogen bonding between the coordinated carboxylate and methanol of adjacent dimmers of **2** leads to the formation of a supramolecular chain along the crystallographic a-axis. Detail photophysical investigations of the ligands in solution and that of the complexes in solid state have been performed to search the origin of emission. Both the complexes are good fluorescent probes and are thermally stable enough to be served as potentially photoactive materials.

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Appendix A. Supplementary data

CCDC 890126 and 890127 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.

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