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Synthesis and spectral studies of the mesogenic Schiff-base, *N*,*N*′-di-(4′-pentyloxybenzoate) salicylidene-1,8-diamino-3,6-dioxaoctane and crystal structure of the Zn(II) complex

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Abstract

A novel Schiff-base, *N*,*N*′-di-(4′-pentyloxybenzoate)salicylidene-1,8-diamino-3,6-dioxaoctane (H_2L_4) with the mesogenic phase, *nematic droplets*, was prepared and its structure studied by elemental analyses and mass, NMR and IR spectra. The di-negative tetra-dentate bonding of the Schiff-base in the non-mesogenic complex, [ZnL_4], as implied on the basis of IR and NMR spectral data, was confirmed in the crystal structure of the monomeric tetrahedral Zn(II) complex. As per the crystal structure of the complex, the dinegative species of the ligand, L_4^{2-}, coordinates to the Zn(II) ion through two phenolate oxygens and two azomethine nitrogens, rendering the overall geometry around Zn(II) to distorted tetrahedron.

Keywords: Mesogenic Schiff-base; Tetrahedral zinc(II) complex; Crystal structure; NMR spectra

1. Introduction

Liquid crystals with transition metal core groups are increasingly a topic of investigation since metals can impart useful shapes and properties which are not easily produced in totally organic liquid crystals [1]. A major distinction between metallomesogens and most organic mesogens is the greater tendency in the former type to exhibit intermolecular dative coordination in the solid state [1]. However, it should be noted that rigid tetrahedral molecules usually seem to prevent mesophase formation [2]. As a part of our investigation on systematic structural and spectroscopic studies of 3d metal complexes of a series of mesogenic organic Schiff-bases, we report here, synthesis and spectroscopic studies on the mesogenic Schiff-base, *N*,*N*′-di-(4′-pentyloxybenzoate)salicylidene-1,8-diamino-3,6-dioxaoctane (H_2L_4) and crystal structure of the corresponding Zn(II) complex. We have observed that despite the mesogenic behaviour of the [CuL_4] (unpublished work), the zinc homologue, [ZnL_4], does not exhibit liquid crystalline properties presumably due to the tetrahedral coordination of the latter [2].

2. Experimental

2.1. Materials

All reagents were purchased from the following and used as received: 4-hydroxy benzoic acid, 1-bromopentane, 2,4-dihydroxy benzaldehyde, *N*,*N*′-dicyclohexylcarbodiimide (DCC), *N*,*N*-dimethylaminopyridine (DMAP) and 1,8-diamino-3,6-dioxaoctane from Sigma–Aldrich, USA, and $Zn(OAc)_2 \cdot 2H_2O$ and KOH from Merck. The solvents received from commercial sources were used as such without further purification and were dried using standard methods [3] when required.

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2.2. Synthesis

The synthesis of *N*,*N*′-di-(4′-pentyloxybenzoate)-salicylidene-1,8-diamino-3,6-dioxaoctane (H_2L_4) (**3**), was achieved by proceeding through three major steps, viz., alkylation of 4-hydroxy benzoic acid with *n*-pentyl bromide, followed by esterification and Schiff-base formation; all the experimental details are given in Scheme 1.

2.2.1. Preparation of 4-pentyloxybenzoic acid (*1*)

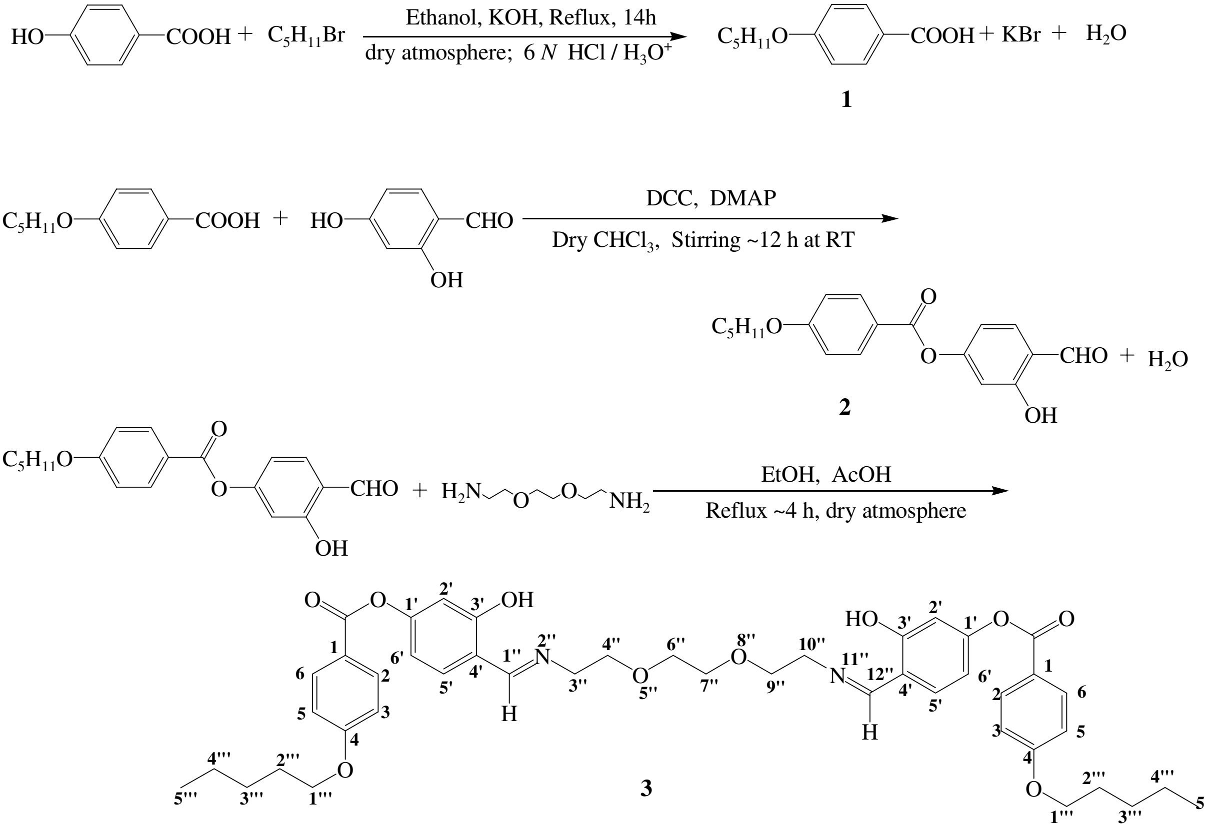
Solutions of 4-hydroxybenzoic acid (11.05 g, 80 mmol) in dry ethanol (150 mL) and of KOH (8.97 g, 160 mmol) in dry ethanol (50 mL) were magnetically stirred with simultaneous drop-wise addition of 1-bromopentane (10.00 mL, 80 mmol). The reaction mixture was refluxed for ~14 h under dry atmosphere and allowed to come to room temperature. The solid alkoxy potassium salt thus obtained was separated out by filtration under suction and treated with dilute HCl until the pH of the reaction mixture reached to ~2. The crude solid white product was filtered off, washed thoroughly with water and recrystallized successively from solutions of glacial acetic acid and toluene. Yield: 11.65 g (70%).

2.2.2. Preparation of 4-pentyloxy (4′-formyl-3′-hydroxy)-benzoate (*2*)

Solutions of 4-pentyloxy benzoic acid (10.40 g, 50 mmol in 50 mL), 2,4-dihydroxybenzaldehyde (6.90 g, 50 mmol in 50 mL), DCC (11.35 g, 55 mmol in 100 mL) in dry chloroform along with solid DMAP (0.3 g, 2.5 mmol as a catalyst) were magnetically stirred at room temperature for ~12 h. The byproduct (dicyclohexyl urea) was filtered off under suction and the solvent was removed on rotavapor. The crude product was recrystallized from hot solution of ethanol and purified by column chromatography over SiO_2 by eluting with a mixture of *n*-hexane and chloroform (v/v, 1:1); evaporation of this eluent yielded the ester, **2**, in the form of a white solid. Yield: 10.17 g (62%).

2.2.3. Synthesis of *N*,*N*′-di-(4′-pentyloxybenzoate)-salicylidene-1,8-diamino-3,6-dioxaoctane (*3*)

Absolute ethanolic solutions of 4-pentyloxy-(4′-formyl-3′-hydroxy)benzoate (6.56 g, 20 mmol, in 100 mL) and 1,8-diamino-3,6-dioxaoctane (1.50 mL, 10 mmol in 20 mL) were refluxed for ~4 h in presence of a few drops of acetic acid and the resultant solution was left over-night in the reaction flask at room temperature. The micro-crystalline yellow coloured product, **3**, was suction-filtered, thoroughly washed with ethanol, recrystallized from a solution of absolute ethanol/chloroform (v/v, 1/1) and dried at room temperature. Yield: 4.61 g (60%); m.p., 110 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 0.945$ (t, $^3J_{H\text{–}H} = 6.9$ Hz, 3H, CH_3), 1.847–1.390 (m, 6H, $H^{methylene}$), 3.614 (s, 2H, $H_{6''}$), 3.721 (s, 4H, $H^{3'',4''}$), 4.035 (t, $^3J_{H\text{–}H} = 6.6$ Hz, 2H, $H^{1'''}$), 6.720 (dd,



Scheme 1. Major reaction steps involved in the synthesis of *N*,*N*′-di-(4′-pentyloxy-benzoate)salicylidene-1,8- diamino-3,6-dioxaoctane (**3**) (H_2L_4).

$^{3}J_{\text{H–H}} = 6.3$ Hz, $^{4}J_{\text{H–H}} = 2.1$ Hz, 1H, H$^{6'}$), (d, $^{4}J_{\text{H–H}} = 1.8$ Hz, 1H, H$^{2'}$), 6.970 (d, $^{3}J_{\text{H–H}} = 8.7$ Hz, 1H, H^{3}), 7.277 (d, $^{3}J_{\text{H–H}} = 8.4$ Hz, 1H, H$^{5'}$), 8.126 (d, $^{3}J_{\text{H–H}} = 9.0$ Hz, 1H, H^{2}), 8.324 (s, 1H, N=CH), 13.813 (s, 1H, ϕ-OH) ppm. *FAB Mass*: the molecular ion (*m*/*e*, 769; 75% intensity) generates simultaneously four fragments, M$_1$–M$_4$, (*m*/*e*, fragment, % intensity): M$_1$: 398, $C_5H_{11}OC_6H_4COOC_6H_3(OH)CH{=}N(CH_2)_2OCH_2\text{-}CH_2^+$, 15; M$_2$: 370, $C_5H_{11}OC_6H_4COOC_6H_3(OH)CH{=}N(CH_2)_2O^+$, 11%; M$_3$: 340, $C_5H_{11}OC_6H_4COOC_6H_3(OH)\text{-}CH{=}NCH_2^+$, 12; M$_4$: 191, $C_5H_{11}OC_6H_4CO^+$, 100; M$_{4'}$ (generated from M$_4$): 121, $HOC_6H_4CO^+$, 97. IR (CCl$_4$, cm^{-1}): ν(O–H)$_{\text{phenol}}$ 3450b, ν(>C=O) 1742, ν(C=N) 1633, ν(C–O)$_{\text{phenol}}$ 1248, ν(C(O)O) 1149; (KBr, cm^{-1}): ν(O–H)$_{\text{phenol}}$ 3439b, ν(>C=O) 1722, ν(C=N) 1628, ν(C–O)$_{\text{phenol}}$ 1246, ν(C(O)O) 1145. *Anal.* Calc. for $C_{44}H_{52}N_2O_{10}$(768.0): C, 68.75; H, 6.77; N, 3.65. Found: C, 68.62; H, 6.50; N, 3.62%.

2.2.4. Synthesis of the zinc complex, [ZnL$_4$]

Anhydrous solutions of *N*,*N*′-di-(4′-pentyloxybenzoate)salicylidene-1,8-diamino-3,6-dioxaoctane (**3**), (0.77 g, 1.0 mmol) in dichloromethane (30 mL) and of zinc acetate (0.22 g, 1.0 mmol) in ethanol (20 mL) were refluxed for ~6 h and the reaction mixture left over-night in the reaction flask after reducing the volume to ~10 mL. The crude solid complex, [ZnL$_4$], was filtered off under suction, washed repeatedly with cold ethanol, recrystallised from the solution of chloroform/ethanol and dried over fused CaCl$_2$ in a desiccator. Yield: 0.68 g (82%); m.p. 210 °C. ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C, TMS): $\delta = 0.947$ (t, $^{3}J_{\text{H–H}} = 6.9$ Hz, 3H, CH$_3$), 1.850–1.392 (m, 6H, H$^{\text{methylene}}$), 4.040 (t, $^{3}J_{\text{H–H}} = 6.9$ Hz, 2H, H$^{1'''}$), 6.973 (d, $^{3}J_{\text{H–H}} = 8.1$ Hz, 1H, H^{3}), 7.185 (d, $^{3}J_{\text{H–H}} = 8.4$ Hz, 1H, H$^{5'}$), 8.133 (d, $^{3}J_{\text{H–H}} = 7.8$ Hz, 1H, H^{2}), 8.197 (s, 1H, N=CH) ppm. IR (KBr, cm^{-1}): ν(>C=O) 1730, ν(C=N) 1535, ν(C–O)$_{\text{phenol}}$ 1253, ν(C(O)O) 1151. *Anal.* Calc. for $C_{44}H_{50}N_2O_{10}Zn$ (832.23): C, 63.50; H, 6.06; N, 3.37; Zn, 7.86. Found: C, 63.27; H, 6.01; N, 3.22; Zn, 7.79%.

2.3. Physical measurements

Infrared spectra were recorded on a JASCO-5300 FT IR spectrophotometer and the ^{1}H and ^{13}C NMR spectra were recorded on a JEOL AL300 FT NMR spectrometer. Mass spectra were recorded on JEOL SX-102 (EI/CI/FAB) mass spectrometers. C, H, and N were micro-analyzed on Elementar Vario EL III Carlo Erba 1108 analyzer.

2.4. X-ray crystallographic data collection and refinement of the structure

X-ray data for the compound ZnL$_4$, [aq74m], was collected at room temperature using a Bruker Smart Apex CCD diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) with ω-scan method. Preliminary lattice parameters and orientation matrices were obtained from four sets of frames. Unit cell dimensions were determined from the setting angles of 7224 reflections in the range of $2.31° < \theta < 24.66°$. Integration and scaling of intensity data was accomplished using SAINT program [4]. The structure was solved by direct methods using SHELXS97 [5] and refinement was carried out by full-matrix least-squares technique using SHELXL97 [5]. Anisotropic displacement parameters were included for all non-hydrogen atoms. All other hydrogen atoms were positioned geometrically and treated as riding atoms, with C–H distances in the range of 0.93–0.96 Å and with U_{iso}(H) values of $1.5U_{\text{eq}}$(C) for methyl hydrogens and $1.2U_{\text{eq}}$(C) for other hydrogen atoms. The geometries of the atoms C17, C18 and C19 were restrained, where distances C17–C18=C18–C19 were set to the target value, 1.55 Å.

3. Results and discussion

3.1. Spectral investigation

The Schiff-base ligand (H$_2$L$_4$), **3**, is yellow-coloured while the Zn(II) complex, [ZnL$_4$] is colourless. Both

Table 1
Crystal data and structure refinement for aq74m, [ZnL$_4$]

Empirical formula	$C_{44}H_{50}N_2O_{10}Zn$
Formula weight	832.23
Cell axes	
a (Å)	8.7660 (6)
b (Å)	41.322(3)
c (Å)	11.5379(8)
Cell angles	
α (°)	90.000 (0)
β (°)	99.358 (1)
γ (°)	90.000 (0)
Cell volume *V* (Å)^3	4123.8 (5)
Crystal system	monoclinic
Crystal size	0.22 × 0.17 × 0.09 mm
Temperature (K)	294(2)
Wavelength (Å)	0.71073
Space group	$P2_1/n$
F(000)	1752
Density (Mg/m^3)	1.340
No. form Unit *Z*	4
Absorption coefficient (mm^{-1})	0.656
Reflections collected/unique	39614/7261 [*R*(int) = 0.0251]
Completeness to $\theta = 25.00$	100.0%
Absorption correction	none
Refinement method	full-matrix least-squares on F^2
Data/restraints/parameters	7261/2/515
$H_{\text{min,max}}$	−10, 10
$K_{\text{min,max}}$	−49, 49
$L_{\text{min,max}}$	−13, 13
$\Theta_{\text{min,max}}$	0.99, 25.0
Goodness-of-fit on F^2	1.193
Final *R* indices	$[I > 2\sigma(I)]$ $R_1 = 0.0468$, $wR_2 = .1259$
R indices (all data)	$R_1 = 0.0540$, $wR_2 = 0.1338$
Largest diffraction peak and hole (e Å^{-3})	0.682 and −0.553

the parent ligand and the metal complex are soluble in chloroform, dichloromethane, DMF and DMSO but are insoluble in water, methanol, ethanol, and acetonitrile. The structures and purities of the Schiff-base ligand, **3**, and of the metal complex, [ZnL_4], were confirmed by IR and ^{1}H NMR spectroscopy and elemental analyses. The structure of the ligand was further confirmed by FAB Mass spectrum. The mass spectral features of H_2L_4 were characterized by the base peak ($m/e = 191$ corresponding to the fragment, $C_5H_{11}OC_6H_4CO^+$), the molecular ion peak with ~75% intensity ($m/e = 769$) and the major fragment peaks ($m/e = 398$, 370, 340, 121) due to $C_5H_{11}OC_6H_4COOC_6H_3(OH)CH{=}N(CH_2)_2OCH_2CH_2^+$, $C_5H_{11}OC_6H_4COOC_6H_3(OH)CH{=}N(CH_2)_2O^+$, $C_5H_{11}OC_6H_4COOC_6H_3(OH)CH{=}NCH_2^+$ and $HOC_6H_4CO^+$. A comparison of the ^{1}H and $^{13}C\{^1H\}$ NMR spectral data of the ligand with those of the Zn(II) complex shows the absence of the phenolic–OH signal (13.813 ppm in H_2L_4) and a significant shift (8.324–8.197 ppm) in the peak position of the –N=C*H* in the spectrum of the metal complex, which implies bonding through the phenolate anion and the azomethine nitrogen atom [6] of the ligand to the metal ion. Similar shifts observed in the $^{13}C\{^1H\}$ NMR spectra were of considerable magnitude in the case of the carbon atoms directly attached to the bonding atoms (phenolate–O and azomethine–N) while those observed for the carbons close to the bonding atoms were of lesser magnitude. Thus, the NMR spectral data imply tetradentate bonding of H_2L through the two $\rangle$C=N groups and two phenolate oxygen atoms. In the IR spectrum of H_2L_4 the broad absorption centered on 3439 and 3450 cm^{-1}, in the solid and solution states, respectively, may be assigned to the O–H stretching vibration of the phenolic group [7]. The strong intensity band occurring at 1633 cm^{-1} may be assigned [8] to ν(C=N) absorption of the azomethine moiety. The strong bands occurring at 1722 cm^{-1} and 1145 cm^{-1} in the solution state of the parent ligand may be assigned [7] to ν(>C=O) and ν(C–O) stretching modes of aromatic ester. The characteristic response of ether in the infrared is associated with the stretching vibration of the C–O–C system. The bands appearing at 1246 and 1064 cm^{-1} may be assigned [7] to ν_{as}(C–O–C) and ν_s(C–O–C) stretching of aryl alkyl ether. Bonding of the parent ligand with the metal ions through phenolate oxygen and azomethine nitrogen was inferred [8] on the basis of (i) disappearance of the ν(O–H) (phenolic) band, and (ii) bathochromic shifts observed in the ν($\rangle$C=N) frequencies in the spectra of the metal complexes.

3.2. Crystal structure and molecular association

The crystal data and structure refinement details for [ZnL_4], [aq74m], are given in Table 1. The molecular structure and atomic labeling scheme of the complex, [ZnL_4], is as shown in Fig. 1.

As per the crystal structure of the complex, the ligand, H_2L_4, coordinates to the Zn(II) ion through two phenolate oxygens (O(1), O(5)) and two azomethine nitrogens (N(1), N(2)), rendering the overall

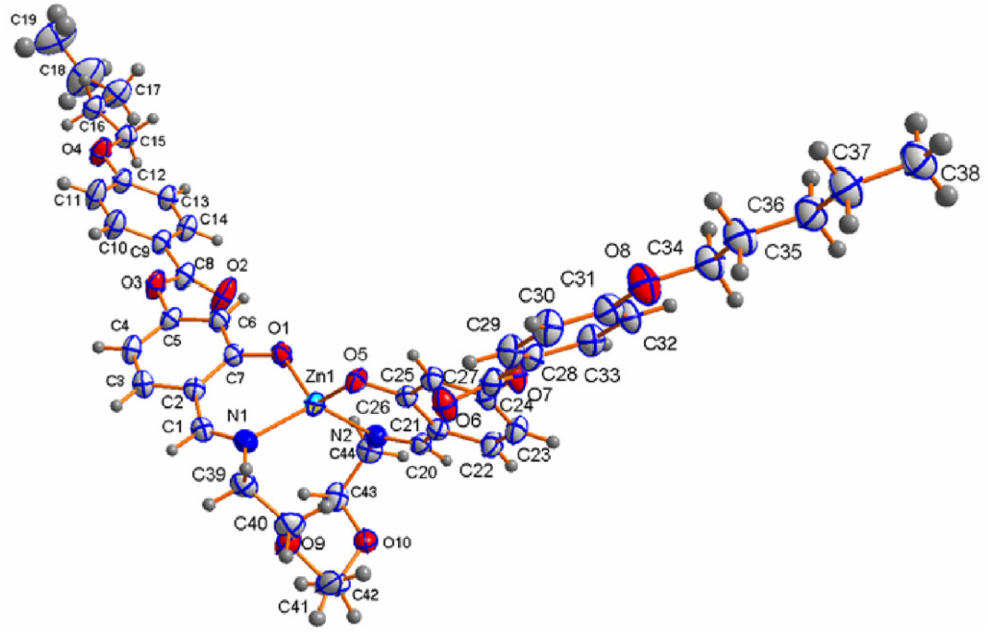


Fig. 1. Molecular structure and atomic labeling scheme of the Complex [ZnL_4].

Table 2
Bond lengths (Å) and angles (°) involved in the tetrahedral unit of the complex [ZnL_4]

N(1)–Zn(1)	2.003(2)	N(2)–Zn(1)	1.994(2)
O(1)–Zn(1)	1.9146(19)	O(5)–Zn(1)	1.9213(18)
O(1)–Zn(1)–O(5)	121.12(9)	O(1)–Zn(1)–N(2)	107.78(9)
O(5)–Zn(1)–N(2)	96.78(8)	O(1)–Zn(1)–N(1)	95.86(9)
O(5)–Zn(1)–N(1)	111.10(9)	N(2)–Zn(1)–N(1)	126.37(9)

Table 3
Hydrogen bonds geometry (Å, °) for the complex [ZnL_4]

D–H...A	*d*(D–H)	*d*(H...A)	*d*(D...A)	*d*(D...A)
C(30)–H(30)...O2[i]	0.93	2.53	3.232(14)	132
C(39)–H(39B)...O10[i]	0.97	2.47	3.350(4)	151

Symmetry code: (i) $1/2 + x$, $1/2 - y$, $1/2 + z$.

geometry around Zn(II) to distorted tetrahedron where the bond lengths and the bond angles are as shown in Table 2. The hydrogen bond geometry is tabulated in Table 3. The crystal structure is stabilized by intermolecular C–H···O interactions which exist between the atom C(30) of the benzoate ring and the carbonyl oxygen atom O(3). Similarly, the aliphatic atom C(39) forms an intermolecular C–H···O interaction with the ethereal oxygen atom O(10), thereby forming an infinite glide-related chain running along crystallographic *c*-axis. The packing diagram is depicted in Fig. 2. Considerable torsion has been observed between benzoate ring and salicylaldimine ring on either side of the metal atom.

4. Conclusion

The Schiff-base, *N*,*N*′-di-(4′-pentyloxybenzoate)salicylidene-1,8-diamino-3,6-dioxaoctane (H_2L_4) with the mesogenic phase, nematic droplets, coordinates to Zn(II) as a di-negative tetra-dentate species, to yield the non-mesogenic tetrahedral complex, [ZnL_4]. As per the crystal structure of the complex, the dinegative species of the ligand, L_4^{2-}, coordinates to the Zn(II) ion through two phenolate oxygens and two azomethine nitrogens, rendering the overall geometry around Zn(II) to distorted tetrahedron.

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Appendix A. Supplementary material

CCDC 649423 contain the supplementary crystallographic data for this paper. 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. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2007.09.002.

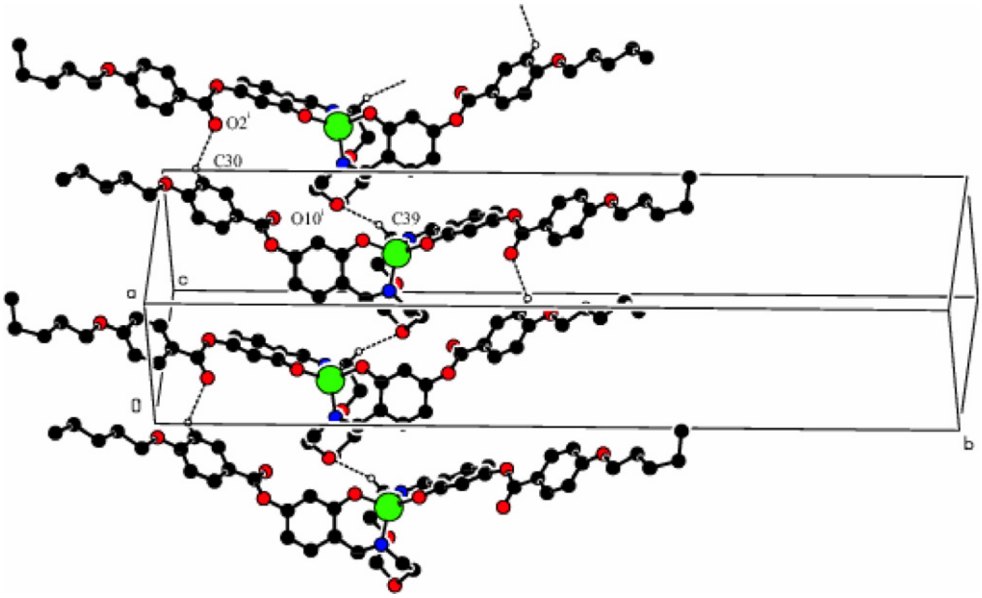

Fig. 2. Part of the crystal structure for [ZnL_4], viewed down *a*-axis. Dashed lines indicate C–H···O interaction. H atoms not involved in hydrogen bonding have been omitted for clarity.

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