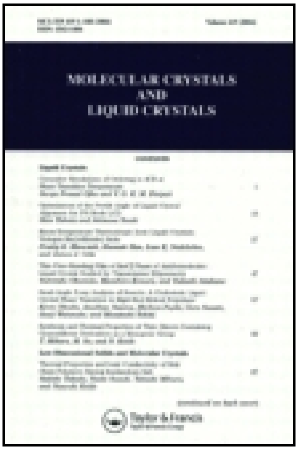

Molecular Crystals and Liquid Crystals

Thermotropic Mesomorphism in Salen-like Zinc Complexes

Iolinda Aiello [a] , Anna Bellusci [a] , Alessandra Crispini [a] , Mauro Ghedini [a] , Daniela Pucci [a] & Tania Spataro [a]

[a] Centro di Eccellenza CEMIF.CAL-LASCAMM, Unità INSTM della Calabria, Dipartimento di Chimica, Università della Calabria, Italy

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Thermotropic Mesomorphism in Salen-like Zinc Complexes

Iolinda Aiello, Anna Bellusci, Alessandra Crispini, Mauro Ghedini, Daniela Pucci, and Tania Spataro
Centro di Eccellenza CEMIF.CAL-LASCAMM, Unità INSTM della Calabria, Dipartimento di Chimica, Università della Calabria, Italy

The reaction between a series of non mesogenic tetradentate salen-like Schiff bases and Zn(II) acetate gives rise to the formation of liquid cristalline complexes showing nematic and smectic phases stable over a quite large temperature range. A dimeric structural arrangement could favour the appearance of such type of mesophase in the case of 1,3-diaminopropane and 1,3-diamino-2,2-dimethylpropane bridges containing ligands while for the salen derivatives a monomeric solvent-induced pentacoordinated arrengement observed in solution and in the crystalline molecular structure, probably prevent the liquid crystalline behaviour.

Keywords: metallomesogens; salen-like Schiff bases; zinc complexes

INTRODUCTION

Metal salen-type complexes constitute a class of coordination compounds which are strategic in catalysis [1] and material chemistry [2], due to their chemical stability, versatility in the structure and in the coordination modes and photophysical properties. However, little work has been done on tetradentate Schiff base complexes of Zn(II) despite zinc derivatives are required for optoelectronic applications [3]. The introduction of a further property such as liquid cristallinity in these systems could be a winning opportunity for achieving new nanostructured functional materials for which combination of order

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Address correspondence to Iolinda Aiello, Centro di Eccellenza CEMIF.CAL-LASCAMM, Unità INSTM della Calabria, Laboratorio Regionale Licryl, CNR-INFM Dipartimento di Chimica, Università della Calabria, I-87030 Arcavacata (CS), Italy. E-mail: iolinda.aiello@unical.it

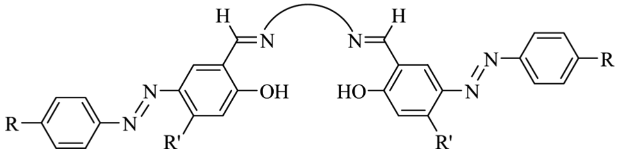


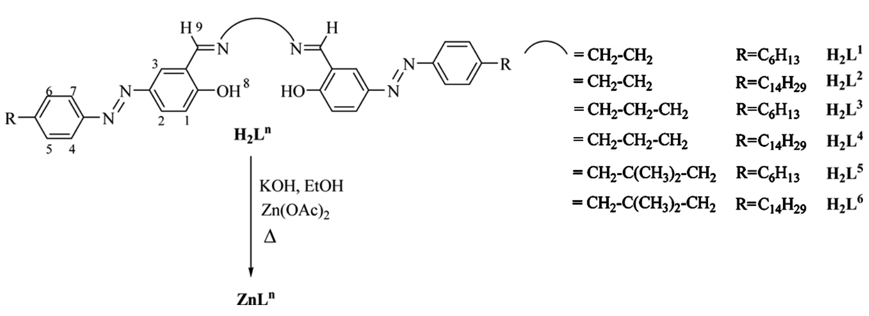
CHART 1 General formula of ligands H_2(salen-n).

and mobility helps the molecular organization to change in reply to any external stimuli.

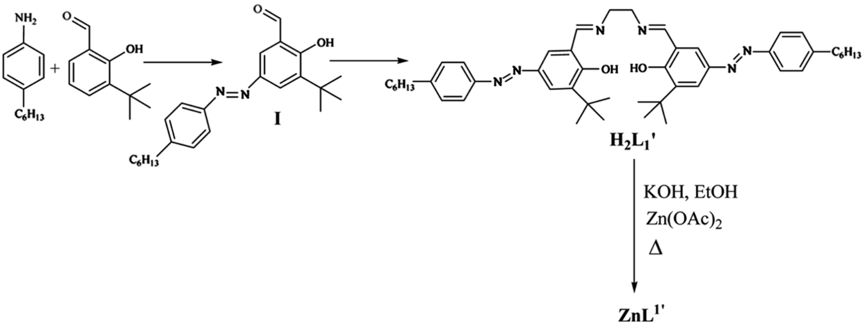
In our previous studies devoted on the correlations between molecular structures, symmetry prerequisites, mesomorphic and physical properties of metallomesogens, we have reported on ligands whose molecular structure combines different functionalities such as a photoisomerizable fragment (an azobenzene group) and a bis-salicylaldehyde H_2(salen-n) cavity capable to host a metal ion (Chart 1) [4].

For this class of ligands the coordination of Cu(II), VO(IV) and Ni(II) promoted mesomorphism (nematic and smectic phases) confirming the role of the metal centers in the synthesis of structures whose molecular architecture can be controlled by the modulation of different and tunable synthons.

Very few examples of mesomorphic Zn(II) complexes reported up to now are based on dithiobenzoate [5], terpyridine [6] or 2,6-bis-[3′,4′,5′-tri(alkoxy)phenyliminomethyl]pyridines ligands [7] or on porphyrin and phtalocyanine derivatives in which the Zn(II) centre shows both a trigonal-bipyramidal geometry or a square planar geometry when incorporated in the cycle [5,8]. Only very recently two examples of Zn(II) derivatives showing the rigid tetrahedral geometry, usually considered to prevent mesophase formation [9],



SCHEME 1 Synthesis, general formula and proton numbering scheme of the **ZnL^n** complexes.



SCHEME 2 Synthesis and general formula of the $\mathbf{H_2L^{1'}}$ ligand and the $\mathbf{ZnL^{1'}}$ complex.

has been reported. In particular, in one case the molecular organization in the columnar mesophase is mainly driven by intermolecular attractive interactions which allow to the half-disc shaped hexacatenar 4,4′-disubstituted-2,2′-bipyridine based zinc complexes to self-assembly into full disc shaped supramolecules [10]. In the other one, the smectic mesomorphism has been keep in pyrazole dimers where the Zn(II) centre is included in a seven membered ring with a flexible spacer which minimize the steric demands of the tetrahedral coordination [11].

With this in mind, we aimed to explore the ability of tetradentate salen-like Schiff bases in the induction of thermotropic mesomorphism upon complexation to the Zn(II) centre. Herein we report the synthesis and the thermal characterization of a series of Zn(II) complexes with non mesogenic bis-(alkylphenylazo)-substituted N,N′-salicylidenediamines $\mathbf{H_2L^{1-6}}$ containing different diamines (namely 1,2-diaminoethane, 1,3-diaminopropane, 1,3-diamine-2,2-dimethylpropane) (Scheme 1). Moreover, in order to clarify the molecular structure of these systems, the single crystal X-ray analysis has been performed on the model compound $\mathbf{ZnL^{1'}}$(Scheme 2) obtained from the $\mathbf{H_2L^{1'}}$ ligand containing *tert*-butyl groups adjacent to the hydroxylic groups.

EXPERIMENTAL SECTION

Measurements

Infrared spectra were recorded on a Spectrum One FT-IR Perkin-Elmer spectrometer and ^{1}H NMR spectra at 300 K on a Bruker AVANCE-300 spectrometer, with TMS as internal standard. Elemental analyses were performed with a Perkin-Elmer 2400 analyzer. The textures of the mesophases were studied with a Zeiss Axioscope polarizing microscope equipped with a CalCTec (Italy) variable heating stage. The transition temperatures and enthalpies were measured on a Perkin-Elmer Pyris 1 Differential Scanning Calorimeter with a heating and cooling rate of 10°C/min. The apparatus was calibrated with indium. Two or more heating/cooling cycles were performed on each sample.

The powder X-ray diffraction patterns were obtained by using a Bruker AXS General Area Detector Diffraction System (D8 Discover with GADDS) with Cu Kα radiation; the high sensitive area detector was placed at a distance from the sample of 10 cm and equipped with a CalCTec (Italy) heating stage. The samples were heated at a rate of 5.0°C min^{-1} to the appropriate temperature. Measurements were performed by charging samples in Lindemann capillary tubes with inner diameter of 0.07 mm.

Single crystal X-ray data were collected on a Bruker-Nonius X8 Apex CCD area detector equipped with graphite monochromator and Mo-Kα radiation ($\lambda = 0.71073$), and data reduction was performed using the SAINT programs; absorption corrections based on multiscan were obtained by SADABS [12]. Details of the crystal data collection are listed in Table 1.

The structure was solved by Patterson method (SHELXS/L program in the SHELXTL-NT software package) [13] and refined by full-matrix least squares based on F^2. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were included as idealized atoms riding on the respective carbon atoms with C−H bond lengths appropriate to the carbon atom hybridization.

Preparation

All reagents and solvents were used as supplied by Sigma-Aldrich Chemical Co. The ligands $\mathbf{H_2L^{1\text{–}6}}$ were synthesized as described in the literature [4]. For the $\mathbf{ZnL^6}$ derivative the ^{1}H NMR spectra are lacking for solubility problems.

TABLE 1 Selected Bond Distances and Angles for Complex $\mathbf{ZnL^{1'}\cdot CH_3OH}$

Zn–O(2)	1.965 (3)	Zn–O(1)	1.969 (3)
Zn–N(4)	2.062 (3)	Zn–N(1)	2.070 (3)
Zn–O(3)	2.081 (3)		
O(2)–Zn–O(1)	96.0 (1)	O(2)–Zn–N(4)	89.2 (1)
O(1)–Zn–N(4)	165.0 (1)	O(2)–Zn–N(1)	146.6 (1)
O(1)–Zn–N(1)	88.3 (1)	N(4)–Zn–N(1)	79.7 (1)
O(2)–Zn–O(3)	109.3 (1)	O(1)–Zn–O(3)	95.9 (19)
N(4)–Zn–O(3)	95.7 (1)	N(1)–Zn–O(3)	103.2 (1)

Synthesis of the intermediate, I

The 4-hexylaniline (1.24 g, 7 mmol) is dissolved in a solution (15 mL) of H_2O containing HCl (12 M, 1.41 mL, 16.92 mmol). To the resulting solution, stirred and cooled to 0°C, an aqueous $NaNO_2$ (0.42 g, 6.09 mmol) solution (6 mL) was added dropwise, and the so-formed diazonium chloride was consecutively coupled with 3-*tert*-butyl-2-hydroxybenzaldehyde (0.96 mL, 5.61 mmol), dissolved in 6.5 mL of aqueous 2 N NaOH (0.52 g, 12.97 mmol) solution. The reaction misture was stirred for 1 h at 0°C and then allowed to warm slowly to room temperature. The brown precipitate which formed was filtered, washed several times with H_2O, dissolved in $CHCl_3$ and the resulting solution dried over anhydrous Na_2SO_4. The crude product, **I**, obtained after removal of the solvent under reduced pressure, was purified by column chromatography (SiO_2, diethyl ether/n-hexane, 1/9 v/v). Brown solid. Yield: 27%. Mp 60–64°C. IR (KBr, cm^{-1}): ν 1685 (stretching C=O), 1421 (stretching N=N). ^1H NMR ($CDCl_3$, ppm): δ 12.11 (s, 1H, H^8), 10.00 (s, 1H, H^9), 8.20 (d, J = 2.19 Hz, 1H, H^2), 8.02 (d, J = 2.37 Hz, 1H, H^3), 7.82 (d, J = 8.25 Hz, 2H, $H^{4,7}$), 7.32 (d, J = 8.28 Hz, 2H, $H^{5,6}$), 2.68 (t, J = 7.77 Hz, 2H, H^α,), 0.89 (t, J = 6.9 Hz, 3H, CH_2CH_3,). Anal. Calcd. for $C_{23}H_{30}N_2O_2$: C 75.37 H 8.25 N 7.64; found C 74.99 H 8.12 N 7.35%.

Synthesis of $H_2L^{1'}$

I (500 mg, 1.34 mmol) and 1,2-diaminoethane (0.04 mL, 0.68 mmol) were mixed in ethanol (50 mL) and stirred under reflux for 4 h. The yellow-orange precipitate which immediately formed was filtered, washed with cold ethanol, and vacuum-dried. Yield: 75%. Mp 163–166°C. IR (KBr, cm^{-1}): ν 2956–2854 (stretching C–H aliphatic), 1601 (stretching C=N), 1463 (stretching N=N). ^1H NMR ($CDCl_3$, ppm): δ 14.43 (s, 1H, H^8), 8.52 (s, 2H, H^9), 8.00 (d, J = 1.76 Hz, 2H, H^2), 7.77 (d, J = 8.22 Hz, 4H, $H^{4,7}$), 7.75 (d, J = 1.76 Hz, 2H, H^3), 7.29 (d, J = 8.22 Hz, 4H, $H^{5,6}$), 4.01 (s, 4H, NCH_2), 2.66 (t, J = 7.04 Hz, 4H, H^α), 0.88 (t, J = 6.46 Hz, 6H, CH_2CH_3). Anal. Calcd. for $C_{48}H_{64}N_6O_2$: C 76.15 H 8.52 N 11.10; found C 75.50 H 8.19 N 11.63%.

Synthesis of $ZnL^{1'}$

NEt_3 (0.22 mL, 0.16 mmol) and Zn(II) acetate dihydrate (35.0 mg, 0.16 mmol) were added to a stirred suspension of $\mathbf{H_2L^{1'}}$ (100 mg, 0.16 mmol) in ethanol (15 mL) and then heated to reflux. A red precipitate immediately formed which was stirred under reflux for 4 h, then cooled to room temperature, filtered, and recrystallized from chloroform-methanol. Yield: 67%. Mp 256°C. IR (KBr, cm^{-1}): ν 2956–2854 (stretching C–H aliphatic), 1598 (stretching C=N), 1439 (stretching N=N). ^{1}H NMR ($CDCl_3$): δ 8.10 (s, 2H, H^9), 8.05 (d, J = 2.33 Hz, 2H, H^2), 7.60 (d, J = 8.24 Hz, 4H, $H^{4,7}$), 7.29 (d, J = 2.34 Hz, 2H, H^3), 7.14 (d, J = 8.37 Hz, 4H, $H^{5,6}$), 4.08 (d, J = 12.48 Hz, 2H, NCH_2), 3.94 (d, J = 12.49 Hz, 2H, NCH_2), 2.64 (t, J = 7.54 Hz, 4H, H^α), 0.91 (t, J = 6.73 Hz, 6H, CH_2CH_3).

Synthesis of ZnL^1

KOH (17 mg, 0.31 mmol) and Zn(II) acetate dihydrate (38.0 mg, 0.15 mmol) were added to a stirred suspension of $\mathbf{H_2L^1}$ (100 mg, 0.15 mmol) in ethanol (15 mL) and then heated to reflux. A yellow precipitate immediately formed which was stirred under reflux for 4 h, then cooled to room temperature, filtered, and crystallized from chloroform-methanol. Yield: 70%. Mp > 350°C. IR (KBr, cm^{-1}): ν 2956–2853 (stretching C−H aliphatic), 1603 (stretching C=N), 1470 (stretching N=N). ^{1}H NMR (DMSO-d_6, ppm): δ 8.65 (s, 2H, H^9), 7.89 (d, J = 2.2 Hz, 2H, H^3), 7.80 (dd, 2H, H^2, J = 8.44), 7.68 (d, J = 7.94 Hz, Hz, 4H, $H^{4,7}$), 7.33 (d, J = 7.93 Hz, 4H, $H^{5,6}$), 6.76 (d, J = 9.28 Hz, 2H, H^1), 3.82 (s, 2H, NCH_2), 2.63 (t, J = 7.59 Hz, 4H, H^α), 0.85 (t, J = 7.09 Hz, 6H, CH_2CH_3). Anal. Calcd. for $C_{40}H_{46}N_6O_2Zn$: C 67.84 H 6.55 N 11.87; found C 67.45 H 6.66 N 11.57%.

All homologous compounds were prepared in similar manner. Colours, yields, melting points, ^{1}H NMR and IR data and elemental analyses are as follows.

Synthesis of ZnL^2

Yellow solid. Yield: 72%. Mp > 350°C. IR (KBr, cm^{-1}): ν 2956–2850 (stretching C−H aliphatic), 1606 (stretching C=N), 1426 (stretching N=N). ^{1}H NMR ($CDCl_3$, ppm): ν 8.14 (s, 2H, H^9), 7.99 (dd, J = 10.43 Hz, 2H, H^2), 7.56 (d, J = 7.88 Hz, 4H, $H^{4,7}$), 7.39 (d, 2H, H^3), 7.11 (d, J = 7.63 Hz, 4H, $H^{5,6}$), 6.90 (d, J = 9.15 Hz, 2H, H^1), 4.20 (m, 2H, NCH_2), 4.06 (m, 2H, NCH_2), 2.62 (t, J = 6.87 Hz, 4H, H^α), 0.87 (t, J = 6.74 Hz, 6H, CH_2CH_3). Anal. Calcd. for $C_{56}H_{78}N_6O_2Zn$: C 72.12 H 8.43 N 9.01; found C 72.25 H 8.48 N 8.84%.

Synthesis of ZnL^3

Yellow solid. Yield: 80%. IR (KBr, cm^{-1}): ν 2956–2853 (stretching C−H aliphatic), 1604 (stretching C=N), 1424 (stretching N=N). ^{1}H

NMR (DMSO-d_6, ppm): δ 8.45 (s, 2H, H^9), 7.85 (d, J = 2.49 Hz, 2H, H^3), 7.78 (dd, J = 2.64 Hz, 2H, H^2), 7.67 (d, J = 8.07 Hz, 4H, $H^{4,7}$), 7.32 (d, J = 8.22 Hz, 4H, $H^{5,6}$), 6.71 (d, J = 9.1 Hz, 2H, H^1), 3.81 (t, J = 4.84 Hz, 4H, NCH_2), 2.63 (t, J = 7.63 Hz, 4H, H^α), 2.03 (m, 2H, NCH_2CH_2), 0.85 (t, J = 6.45 Hz, 6H, CH_2CH_3). ^{1}H NMR ($CDCl_3$, ppm): δ 8.29 (s, 2H, H^α), 8.07 (s, 2H, H^α), 7.87 (dd, J = 8.4 Hz, 2H, H^2), 7.73 (m, 4H, $H^{4,7}$), 7.64 (d, J = 7.62 Hz, 2H, H^3), 7.20 (d, J = 8.25 Hz, 4H, $H^{5,6}$), 7.04 (d, J = 9.3 Hz, 2H, H^1), 6.88 (d, J = 9.09 Hz, 2H, H^1), 4.45 (m, 1H, N$-$$CH_2$), 3.81 (m, 1H, N$-$$CH_2$). Anal. Calcd. for $C_{41}H_{48}N_6O_2Zn$: C 68.18 H 6.70 N 11.64; found C 68.53 H 6.61 N 11.90%.

Synthesis of ZnL^4

Orange solid. Yield: 83%. IR (KBr, cm^{-1}): ν 2921–2851 (stretching C$-$H aliphatic), 1604 (stretching C=N), 1425 (stretching N=N). ^{1}H NMR (DMSO-d_6, ppm): δ 8.45 (s, 2H, H^9), 7.84 (d, J = 2.64 Hz, 2H, H^3), 7.78 (dd, J = 9.24 Hz, 2H, H^2), 7.66 (d, J = 8.07 Hz, 4H, $H^{4,7}$), 7.31 (d, J = 8.22 Hz, 4H, $H^{5,6}$), 6.70 (d, J = 9.24 Hz, 2H, H^1), 3.82 (t, 4H, NCH_2), 2.62 (t, J = 7.65 Hz, 4H, H^α), 2.03 (m, 2H, NCH_2CH_2) 0.85 (t, J = 6.45 Hz 6H, CH_2CH_3). Anal. Calcd. for $C_{57}H_{80}N_6O_2Zn$: C 72.32 H 8.52 N 8.88; found C 72.71 H 8.19 N 8.91%.

Synthesis of ZnL^5

Orange solid. Yield: 80%. IR (KBr, cm^{-1}): ν 2921–2851 (stretching C$-$H aliphatic), 1604 (stretching C=N), 1425 (stretching N=N). ^{1}H NMR (DMSO-d_6, ppm): δ 8.38 (s, 2H, H^9), 7.86 (d, J = 9.03 Hz, 2H, H^3), 7.79 (dd, J = 9.39 Hz, 2H, H^2), 7.67 (d, J = 8.22 Hz, 4H, $H^{4,7}$), 7.33 (d, J = 8.22 Hz, 4H, $H^{5,6}$), 6.70 (d, J = 9.09 Hz, 2H, H^1), 3.63 (s, 4H, NCH_2), 2.63 (t, J = 7.65 Hz, 4H, H^α). ^{1}H NMR ($CDCl_3$, ppm): δ 8.19 (s, 2H, H^α), 7.98 (s, 1H, H^α), 7.86 (dd, J = 9.01 Hz, 2H, H^2), 7.69 (m, 6H, H^3, $H^{4,7}$), 7.22 (d, 4H, $H^{5,6}$), 6.85 (d, J = 9.16 Hz, 2H, H^1), 7.05 (d, J = 9.42 Hz, 2H, H^1), 4.48 (d, J = 12.34 Hz, 1H, N$-$$CH_2$), 3.31 (d, J = 12.46 Hz, 1H, N$-$$CH_2$), 2.62 (t, 4H, H^α). Anal. Calcd. for $C_{43}H_{52}N_6O_2Zn$: C 68.83 H 6.99 N 11.20; found C 68.54 H 6.82 N 11.37%.

Synthesis of ZnL^6

Orange solid. Yield: 75%. IR (KBr, cm^{-1}): ν 2921–2851 (stretching C$-$H aliphatic), 1604 (stretching C=N), 1425 (stretching N=N). Anal. Calcd. for $C_{59}H_{84}N_6O_2Zn$: C 72.70 H 8.69 N 8.62; found C 72.36 H 8.35 N 8.28%.

RESULTS AND DISCUSSION

Synthesis

New mononuclear zinc complexes $\mathbf{ZnL^{n}}$ have been prepared reacting the corresponding $\mathbf{H_2L^{n}}$ ligands with stoichiometric amounts of Zn(II) acetate dihydrate in ethanolic KOH solutions, giving rise to the final products at yields between 70 and 83%.

The preparation of the new ligand $\mathbf{H_2L^{1'}}$ (Scheme 2) was accomplished by condensation of 1,2-diaminoethane with the **I**, which in turn results from coupling of the diazonium chloride of 4-hexylaniline with 3-*tert*-butyl-2-hydroxybenzaldehyde. The ligand has been complexed with Zn(II) acetate dihydrate to give the corresponding zinc derivative $\mathbf{ZnL^{1'}}$.

Complex molecular structure

The molecular structure of $\mathbf{ZnL^{1'}CH_3OH}$ has confirmed the formation of a monomeric specie, with the Zn(II) ion in a five-coordinated square pyramidal geometry due to the coordination of a methanol molecule in the axial position (Fig. 1). Selected bond distances and angles are reported in Table 1.

Bond lengths and angles are comparable with those found in similar pentacoordinated Zn(II) salen derivatives [14], confirming the tilt of the Zn(II) centre from the basal plane and the distorsion of the geometry from the ideal one.

All complexes have been fully characterized by spectroscopic techniques (IR and ^{1}H NMR) and elemental analysis. By comparing the ^{1}H NMR spectra of the ligands with those of the corresponding Zn(II) complexes the absence of the proton signal corresponding to the phenolic groups in the 12–14 ppm region confirmed the coordination of the metal centre.

It is known that *N,N′*-bis-salicylidene ethylenediamine complexes of Zn(II), unlike their analogous Cu(II) and Ni(II) derivatives show, in the solid state, a five-coordinated geometry around the metal centre,

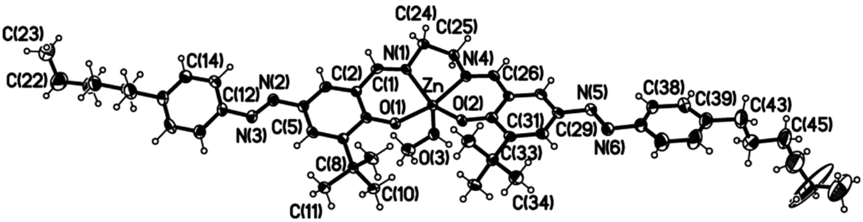


FIGURE 1 Molecular structure and atom numbering scheme for $\mathbf{ZnL^{1'}\cdot CH_3OH}$.

giving rise to derivatives of general formula [Zn(salen)L], where L is a coordinating solvent [14] or a pyridine ligand [15]. In some case, when the solvent does not take place in the coordination sphere, dimeric structures have been described up to now: one, consistent with the formation of five coordinated dimeric units connected through oxobriging salen, $[Zn(salen)]_2$ (**A**, Chart 2) [16] and another one, recovered only with the *tert*-butylated version of the salen ligand, showing a helical structure in which the coordination geometry around the two Zn(II) ions is tetrahedral distorted, $[Zn_2(salen\text{-}^tBu)_2]$ (**B**, Chart 2) [17].

Interestingly, when the alkyl chain between the two imine moieties increases in length ($n \geq 3$), a greater propensity to form bimetallic systems through oxygen-bridging has been observed, whereas in the presence of steric demanding groups in 3,3′ position a monomeric geometry around the five-coordinate Zn(II) centre is preferred [15,18].

Bond lengths and angles are comparable with those found in similar pentacoordinated Zn(II) salen derivatives [14], confirming the tilt of the Zn(II) centre from the basal plane and the distorsion of the geometry from the ideal one. This trend is in line with the behaviour observed for the present complexes.

The presence of azo moieties in the molecular structure does not provide an identification of the conformational geometries around the zinc centre using UV-Vis spectroscopic methods [19] but ^{1}H NMR studies, combined with structural reports on the **ZnL**$^{\mathbf{1'}}$ model complex, allowed us to define the structural preferences of Zn(II) towards **HL**$^{\mathbf{n}}$ ligands. The ^{1}H NMR spectra of the salen-Zn complexes **ZnL**$^{\mathbf{1}}$, **ZnL**$^{\mathbf{2}}$, **ZnL**$^{\mathbf{1'}}$ are all consistent with symmetrical monomeric structures in solution, showing only a single sharp resonance for the imine protons H^9 but two distinct signals, as doublets, for the protons of the ethylene linkage, NCH_2. However, in the ^{1}H NMR spectra of

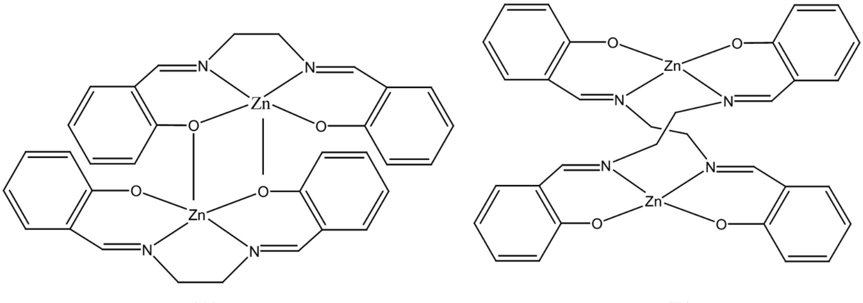


CHART 2 Molecular structure of Zn(II) complexes A and B.

salen derivatives performed in DMSO solution for the the protons of the ethylene linkage, a single resonance is observed as singlet; this is an evidence of the magnetically equivalence of these protons, on the NMR scale, due to the flexibility of the chain which lead the mean positions in the plane, in these experimentally conditions.

The IR spectra suggested the presence of solvent molecules filling the fifth coordination site of the zinc centre.

Extending the alkyl chains by introducing the 1,3-diaminopropane and 1,3- diamine-2,2-dimethylpropane as N,N chelating ring, a drastic change in the structure of the corresponding zinc complexes is observed. The ^{1}H NMR spectra of **ZnL^3–ZnL^6** complexes are consistent with unsymmetric oxygen-bridged dimeric structures (like **A** and **B** in Chart 2), due to the presence of two singlets for both theimine groups and the protons in *ortho* to the coordinated phenolic oxygen atoms.

Mesomorphism

The thermal behaviour of **ZnL^n** compounds have been investigated by DSC and optical microscopy and the results are collected in Table 2.

TABLE 2 Transition Temperatures, Phase Assignments and Enthalpy Changes

Compound	Transition[a]	T [°C]	ΔH [kJmol^{-1}]
ZnL^1	C-I	>350[b]	
ZnL$^{1'}$	C-I	256[b]	
ZnL^2	C-I	>350[b]	
ZnL^3	C-C′	164.5	34.9
	C′-SmC	207.2	7.8
	SmC-N	285.7	11.2
	N-I$_{dec}$	309	
ZnL^4	C-C′	120.2	29
	C′-C″	172.3	1.7
	C″-SmC	192.1	1.3
	SmC-I$_{dec}$	247.7	
ZnL^5	C-C′	130.3	19.2
	C′-SmC	258.6	10
	SmC-I$_{dec}$	305	
ZnL^6	C-C′	50.32	3.47
	C′-C″	90.56	1.22
	C″-SmC	118.07	26.25
	SmC-I$_{dec}$	227[b]	

[a] C: crystal; Sm: smectic; N: nematic; I: isotropic liquid; dec; decomposition.
[b] From optical microscopy.

None of the ligands display thermotropic mesomorphism and upon heating they all melt at temperatures progressively decreasing with both the increase of the bridge length (N = 1 to 3) or the terminal chain length (n = 6 to n = 14), ranging from 211°C for $\mathbf{H_2L^1}$ to 120°C for $\mathbf{H_2L^6}$ [4a]. However, mesophases are induced upon complexation with Zn(II) except for the salen ligands $\mathbf{HL^{1\text{–}2}}$. The different mesophases were recognized through optical observations, even if an unambigous assignment was difficult to gain because of the dark colors of the textures and the high temperature at which the melting points occur. In particular a Schlieren texture has been observed for all complexes, indicative of a Smectic C phase, followed, only in the $\mathbf{ZnL^3}$ complex case, by a Nematic phase which appear just some degrees before the clearing point. Moreover, approaching the transition to the isotropic liquid phase, a considerable amount of decomposition was detected for all complexes (exothermic peaks in the differential scanning colorimeter trace). Hence, variable temperature powder X-ray diffraction (PXRD) investigations were performed only on the mesogens featuring the comparatively higher thermal stability (with respect to decomposition) and lower melting points.

For the higher homologoues, with N = 1,3-diaminopropane; N = 1,3-diamino-2,2-dimethylpropane, a Smectic C (SmC) phase with typical Schlieren textures is observed in the case of $\mathbf{ZnL^4}$ and $\mathbf{ZnL^6}$, and confirmed by PXRD. Both spectra, recorded between 170 and 185°C on heating, revealed only three sharp peaks in the low angle region with a reciprocal space ratio of 1:2:3. The maxima can be assigned to the (001), (002) and (003) reflections of a lamellar arrangement. The layer spacing of the SmC phase is in both cases of 42 Å, in agreement with the previously reported values found for similar Cu(II) and Ni(II) complexes, where the molecular length calculated in the full extended conformation of 56 Å, confirmed the tilted nature of the mesophase [4a]. For all complexes the length of the terminal alkyl chains influences the type of mesophase and the thermal behaviour. Thus, the usual trend is observed: a short chain (C_6H_{13}) induces a nematic phase while a longer one ($C_{14}H_{29}$) causes a more ordered mesophase (SmC) to appear and the clearing temperature decrease with increasing n.

CONCLUSIONS

A series of tetradentate Schiff bases ligands, namely the non mesogenic bis-(alkylphenylazo)-substituted N,N′-salicylidenediamines containing different diamines (N = 1,2-diaminoethane; N = 1,3-diaminopropane; N = 1,3-diamino-2,2-dimethylpropane) have been complexed with equimolar amounts of Zn(II) acetate. With the exception the salen derivatives, all complexes display thermotropic mesomorphism, stable over a quite large temperature range and with the clearing temperatures decreasing as the terminal chains increase in length.

The mesomorphic trend observed for these complexes is strongly correlated to the molecular shape and to the deriving intermolecular forces, which could be easily modulated through the proper choice of the diamine chelate ring size. Indeed, for Zn(II) complexes containing a salen core, the marked preference for the five coordinate pyramidal configuration by coordination of an extra solvent molecule, observed also in presence of bulky groups on both 3 and 3' positions of the Schiff base, induces a globally rigid and dense framework whose disruption need a very big thermal contribution leading to very high melting temperatures. The conformational flexibility induced by virtue of the extra methylene unit, for both the $N-(CH_2)_3-N$ and $N-CH_2-C(Me)_2$ CH_2-N bridges, enables a supramolecular assembly of two or more molecules, aggregated through intermolecular Zn-O interactions, which is beneficial for inducing a mesogenic attitude in the corresponding complexes.

In conclusion, the synthesis of some representative examples of both smectic and nematic Zn(II) complexes containing the free $-N{=}N-$ group has been successfully achieved demonstrating once again that the flexibility in the design of metallomesogens is a very distinctive feature which would have high potentiality to reach easily selected mesomorphic properties suitable for new applications.

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