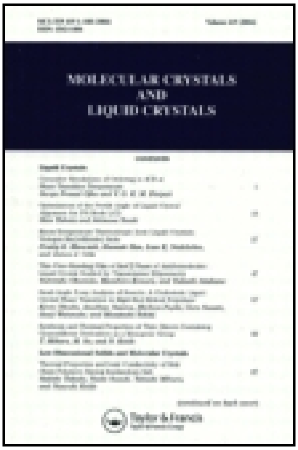

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Copper(II) and Nickel(II) Complexes of a Tetradentate Ligand Containing an N,N′-Bis(Salicylidene)Dodecane-1, 10-Diamine Core

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Version of record first published: 18 Mar 2009

To cite this article: Daniela Pucci, Iolinda Aiello, Anna Bellusci, Giovanna Callipari, Alessandra Crispini & Mauro Ghedini (2009): Copper(II) and Nickel(II) Complexes of a Tetradentate Ligand Containing an N,N′-Bis(Salicylidene)Dodecane-1, 10-Diamine Core, Molecular Crystals and Liquid Crystals, 500:1, 144-154

To link to this article: http://dx.doi.org/10.1080/15421400802714098

Mol. Cryst. Liq. Cryst., Vol. 500, pp. 144–154, 2009
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400802714098

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Copper(II) and Nickel(II) Complexes of a Tetradentate Ligand Containing an N,N′-Bis(Salicylidene)Dodecane-1,10-Diamine Core

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The synthesis of mesomorphic Cu(II) and Ni(II) coordination compounds arising from a new series of tetradentate Schiff bases containing two salicylaldimine fragments connected by a very long spacer,-$(CH_2)_{12}$*-, (*H_2L^n*):* $L^1 = p\text{-}(C_6H_{13}O)\text{-}C_6H_4COO$*,* $L^2 = p\text{-}(C_{12}H_{25}O)\text{-}C_6H_4COO$*, is described. The self-assembly and liquid-crystalline properties of these complexes have been investigated by variable temperature powder X-ray diffraction and the relationship between the global molecular shape and the mesogenic performances is discussed. The reported Cu(II) compounds are molecular materials which could be of interest for applications in the field of magnetic molecule-based devices.*

Keywords: Cu(II) and Ni(II) complexes; metallomesogens; salen-like Schiff bases

INTRODUCTION

Liquid crystals are intriguing functional materials, very important in many applicative fields, including those requiring special electrooptic devices [1]. The idea of introducing paramagnetic ions in liquid crystalline materials has been intensively pursued in the last two decades motivated by several reasons: i) increase applications of one-dimensional

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This work was partly supported by both the Ministero dell'Istruzione, dell'Università e della Ricerca through the Centro di Eccellenza CEMIF.CAL grant and by the Italian PRIN founding n. 2006038447.

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magnets in order to repair defects in their structure, ii) realize alignment or *re* alignment with a very small field, iii) obtain magneto-optic data storage devices. The most of magnetic liquid crystals reported are based on rare-heart ions which offer a large magnetic anisotropy [2], but a number of paramagnetic mesogens have been synthesized also including in the molecular skeleton a d metal as spin source which, coordinated to a diamagnetic ligand, gives rise to a cylindrical, discotic or sphaero symmetrical whole molecular shape depending on the position, nature and number of substituents on the molecular core [3].

In particular, bidentate or tetradentate ligands derived from salicylaldehyde and properly substituted anilines (Schiff bases), are ligands which have been widely used in the synthesis of magnetic metallomesogens. The first calamitic bis-N-(4-substituted)salicylaldiminato Cu(II) and Ni(II) complexes based on bidentate Schiff bases of molecular structure **I** (Chart 1) described by Galyametdinov and co-workers in 1984 [4], were followed by only few examples of Cu(II) and VO(II) mesogens [5–7]. They all show a lamellar smectic mesomorphism, whose investigations by EPR and magnetic susceptibility measurements, enabled some relevant correlations between magnetic properties and molecular structure, regarding, for example, the alignment of the molecules along an external magnetic field.

Though M(salen)-type complexes (salen) = N,N′- ethylenebis(salicylideneiminato) form a class of coordination compounds which are strategic in material chemistry, due to their photophysical properties and their versatility in the structure and in the coordination modes [8], there are very few examples of paramagnetic

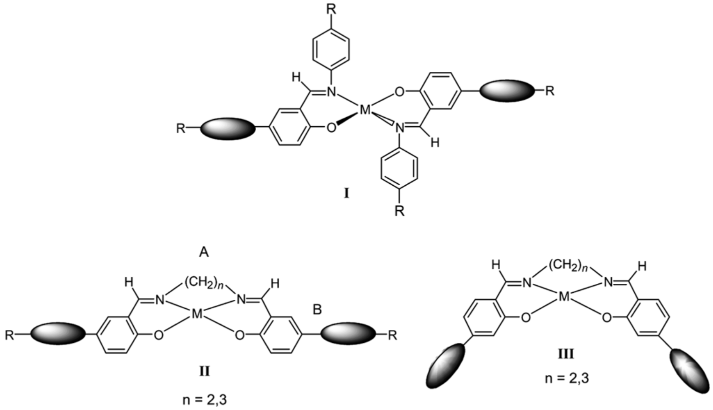


CHART 1 Basic chemical structures of mesomorphic metal complexes of Schiff bases.

metallomesogens based on this kind of tetradentate ligand. Starting from 2-hydroxybenzaldehydes judiciously substituted in 5 position with substituents bearing terminal chains of suitable length, it was possible to synthesize Cu(II) and Ni(II) complexes with the alkylene spacer of 2 or 3 C atoms (salen and salpen respectively), for which the N,N-*cis* metal coordination mode affords to a roughly square planar or square pyramidal coordination geometry, depending on the nature of the metal centre. These metallomesogens show a rod-like molecular shape **II** (Chart 1) promoting calamitic mesomorphism (nematic and smectic phases) but they have very high transition temperatures (higher than 200°C) which prevented any possible applications [9–11].

Since molecular symmetry, packing and mesogenic properties are dramatically influenced by the nature and/or the geometry of peripheral substituents, the effect of the introduction of lateral or unsymmetrical terminal groups has been tested, but they did not find to be relevant in affecting the melting behaviour [12].

On the contrary, the presence of very long C_n ($n > 14$) alkoxy chains at the 4 position of the aromatic rings of salen or salpen-based Cu(II) and VO(IV) complexes gives rise to the molecular shape **III** (Chart 1) which promoted an intriguing (a bilayer mesophase or a lamello-columnar phase) and relatively low melting mesomorphism, driven by the position of the ring substitution as well as by the metal centres [13]. In order to prepare new functional liquid crystals useful for molecule-based magnetic devices, we are interested in studying paramagnetic complexes arising from tetradentate Schiff bases whose thermal, mesomorphic and magnetic properties can be strongly modulated by little changes of single tectons able to deeply influence the molecular geometry, the intermolecular-assembly and ultimately their performances as molecular materials. In particular we have focused our investigations on the modification of some structural elements of the prototypal M(salen-like) molecular structure **II** in Chart 1: i) the length of the central diamine spacer (A) by replacing the short central bridge for a flexible backbone consisting of 12 carbon atoms and ii) the length and the position of the peripheral flexible chains (B). In the present paper we report on the synthesis, characterization and mesogenic properties of two tetradentate Schiff bases, $\mathbf{H_2L^n}$ and of their corresponding Cu(II) complexes. The $\mathbf{H_2L^n}$ like ligands featuring a short central bridge (e.g., 2–4 carbon atoms) display a O,N,N,O cavity which can accomodate metal ions requiring either a tetrahedral (i.e., Cu(II)) or a square planar (i.e., Ni(II)) coordination geometry. In order to test the influence of the metal centre on the thermotropic properties induced by these $\mathbf{H_2L^n}$ ligands on metal ions demanding a different coordination environment the synthesis has been worked up to the homologous Ni(II) compounds.

EXPERIMENTAL SECTION

Measurements

The infrared spectra in KBr were recorded on a Perkin-Elmer Spectrum One FT-IR spectrometer equipped for reflectance measurements. The ^{1}H NMR spectra were recorded on a Bruker WH-300 spectrometer in $CDCl_3$ solutions, with TMS as internal standard. Elemental analyses were performed with a Perkin-Elmer 2400 analyzer.

The textures of the mesophases were studied with a Zeuss Axioscope polarizing microscope equipped with a Linkam C0 600 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 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 20 cm and equipped with a CalCTec (Italy) heating stage. The sampes were heated at a rate of 5.0°C min^{-1} to the appropriate temperature. Measuements were performed by charging samples in Lindemann capillary tubes with inner diameter of 0.5 mm.

Preparation

The preparation of 4-alkoxy-benzoic acid 4-formyl-3-hydroxy-phenyl esters ($\mathbf{I}^1$ and $\mathbf{I}^2$) was accomplished following the synthesis reported in literature [14]. Colours, yields, melting points, IR and ^{1}H NMR data and elemental analyses are as follows.

Synthesis of the Intermediates, I^n

4-hexyloxy-benzoic acid 4-formyl-3-hydroxy-phenyl ester (I^1). White solid. Yield: 0.87 g (38%). Mp: 92°C. IR (KBr): ν 2939–2868 (stretching aliphatic CH), 1738 (ester stretching C=O), 1656 (aldehydic stretching C=O), 1606, 1246 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 11.25 (s, 1H, OH), 9.88 (s, 1H, CH=O), 8.12 (d, 2H, $J = 8.64$ Hz, $H^{2',6'}$), 7.61 (d, 1H, $J = 7.20$ Hz, H^6), 6.98 (d, 2H, $J = 8.64$ Hz, $H^{3',5'}$), 6.93 (d, 1H, $J = 1.92$ Hz, H^3), 6.89 (dd, 1H, $J_{3,5} = 1.92$ Hz/$J_{5,6} = 7.20$ Hz, H^5), 4.05 (t, 2H, $J = 6.72$ Hz, OCH_2), 1.87–0.89 (m, 11H, aliphatic protons) ppm. Anal. Calcd. for $C_{20}H_{22}O_5$: C, 70.16; H, 6.48%. Found: C, 70.01; H, 6.49.

4-dodecyloxy-benzoic acid 4-formyl-3-hydroxy-phenyl ester (I^2). White solid. Yield: 0.65 g (25%). Mp: 78°C. IR (KBr): ν 2956–2851 (stretching aliphatic CH), 1735 (ester stretching C=O), 1681 (aldehydic stretching

C=O), 1608, 1254 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 11.25 (s, 1H, OH), 9.88 (s, 1H, CH=O), 8.12 (d, 2H, $J = 8.54$ Hz, $H^{2',6'}$), 7.61 (d, 1H, $J = 8.54$ Hz, H^6), 6.98 (d, 2H, $J = 8.54$ Hz, $H^{3',5'}$), 6.91 (dd, 1H, $J_{3,5} = 2.44$ Hz/$J_{5,6} = 8.54$ Hz, H^5), 6.88 (d, 1H, $J = 2.44$ Hz, H^3), 4.05 (t, 2H, $J = 6.10$ Hz, OCH_2), 1.82-0.88 (m, 23H, aliphatic protons) ppm. Anal. Calcd. for $C_{26}H_{34}O_5$: C, 73.21; H, 8.03%. Found: C, 71.93; H, 7.57.

Synthesis of H_2L^n

N,N′-bis[(4′-hexyloxy)benzoyloxy benzylidene]-1,12-diaminododecane, H_2L^1. 1,12-Diaminododecane (0.12 g, 0.59 mmol) was added to a hot solution of $\mathbf{I}^1$ (0.5 g, 1.17 mmol) in methanol (15 mL). The precipitate, which immediately formed, was stirred under reflux for 4 h, then filtered and washed with ethanol. The crude product was purified by recrystallization from acetone and then dried *in vacuo*. Yellow solid. Yield: 0.52 g (83%). IR (KBr): ν 2921-2848 (stretching aliphatic CH), 1726 (stretching C=O), 1637 (stretching C=N), 1606, 1253 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 14.13 (s, 2H, OH), 8.30 (s, 2H, CH=N), 8.12 (d, 4H, $J = 7.32$ Hz, $H^{2',6'}$), 7.25 (d, 2H, $J = 7.20$ Hz, H^6), 6.96 (d, 4H, $J = 7.32$ Hz, $H^{3',5'}$), 6.79 (br s, 2H, H^3), 6.71 (d, 2H, $J = 7.20$ Hz, H^5), 4.03 (t, 4H, $J = 7.32$ Hz, OCH_2), 3.585-3.55 (m, 4H, $C{=}NCH_2$), 1.84-0.91 (m, 42H, aliphatic protons) ppm. Anal. Calcd. for $C_{52}H_{68}N_2O_8$: C, 73.56; H, 8.07; N, 3.30%. Found: C, 73.45; H, 7.84; N, 3.66%.

N,N′-bis[(4′-dodecyloxy)benzoyloxy benzylidene]-1,12-diaminododecane, H_2L^2. The $\mathbf{H_2L^2}$ ligand was prepared following the procedure described for $\mathbf{H_2L^1}$. Colour, yield, IR and ^{1}H NMR data and elemental analyses are as follows. Yellow solid. Yield: 0.52 g (88%). IR (KBr): ν 2919–2849 (stretching aliphatic CH), 1727 (stretching C=O), 1638 (stretching C=N), 1606, 1509, 1467, 1253 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 14.13 (s, 2H, OH), 8.31 (s, 2H, CH=N), 8.12 (d, 4H, $J = 8.85$ Hz, $H^{2',6'}$), 7.26 (d, 2H, $J = 7.89$ Hz, H^6), 6.96 (d, 4H, $J = 8.85$ Hz, $H^{3',5'}$), 6.79 (d, 2H, $J = 1.98$ Hz, H^3), 6.71 (dd, 2H, $J_{3,5} = 1.98$ Hz/$J_{5,6} = 7.89$ Hz, H^5), 4.04 (t, 4H, $J = 6.87$ Hz, OCH_2), 3.58 (t, 4H, $J = 6.90$ Hz, $C{=}NCH_2$), 1.85-0.85 (m, 66H, aliphatic protons) ppm. Anal. Calcd. for $C_{64}H_{92}N_2O_8$: C, 75.55; H, 9.11; N, 2.75%. Found: C, 75.59; H, 9.08; N, 2.84%.

Synthesis of Complexes

NiL^1. Nickel acetato tetrahydrate (0.044 g, 0.18 mmol) was added to a hot solution of $\mathbf{H_2L^1}$ (0.15 g, 0.18 mmol) in ethanol (15 mL). The reaction mixture was stirred at reflux for 5 h and then cooled to room temperature. The solid, collected by filtration, was washed with water, ethanol and chloroform and then dried *in vacuo*. Green solid. Yield: 0.12 g (77%). IR (KBr): ν 2924-2853 (stretching aliphatic CH), 1731

(stretching C=O), 1608 (stretching C=N), 1435, 1257 cm^{-1}. Anal. Calcd. for $C_{52}H_{66}N_2O_8Ni$: C, 68.95; H, 7.34; N, 3.09%. Found: C, 69.26; H, 7.14; N, 3.33%.

NiL^2*.* The **NiL^2** complex was prepared following the procedure described for **NiL^1**. Colour, yield, IR and ^{1}H NMR data and elemental analyses are as follows. Green solid. Yield: 0.12 g (77%). IR (KBr): ν 2922–2852 (stretching aliphatic CH), 1728 (stretching C=O), 1618 (stretching C=N), 1606, 1540, 1255 cm^{-1}. Anal. Calcd. for $C_{64}H_{90}N_2O_8Ni$: C, 71.57; H, 8.44; N, 2.61%. Found: C, 71.89; H, 8.44; N, 2.91%.

CuL^1*.* Copper(II) acetate monohydrate (0.029 g, 0.15 mmol) was added to a hot solution of **H$_2$L^1** (0.150 g, 0.15 mmol) in ethanol (15 mL). The reaction mixture was stirred at reflux for 5 h and then cooled to room temperature. The solid, collected by filtration, was washed with water, ethanol and chloroform and then dried *in vacuo*. Green solid. Yield: 0.12 g (76%). IR (KBr): ν 2924-2853 (stretching aliphatic CH), 1730 (stretching C=O), 1606 (stretching C=N), 1542, 1256 cm^{-1}. Anal. Calcd. for $C_{52}H_{66}N_2O_8Cu$: C, 68.58; H, 7.30; N, 3.08%. Found: C, 68.59; H, 7.12; N, 3.28%.

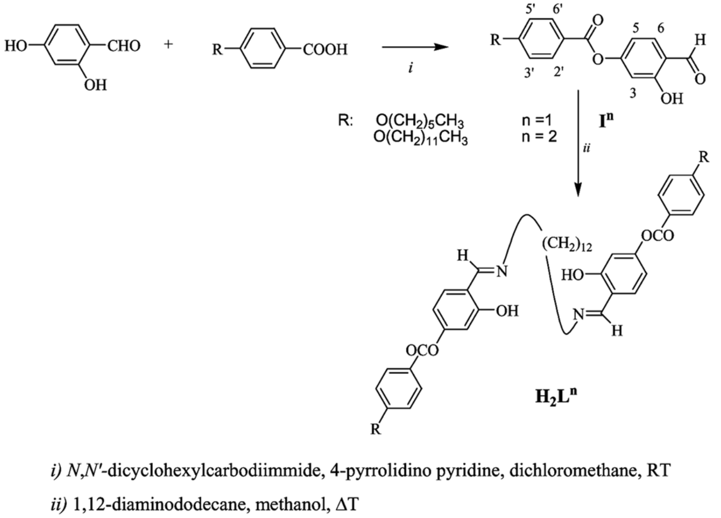
CuL^2*.* The **CuL^2** complex was prepared following the procedure described for **CuL^1**. Colour, yield, IR and ^{1}H NMR data and elemental analyses are as follows Green solid. Yield: 0.12 g (78%). IR (KBr): ν 2923-2852 (stretching aliphatic CH), 1722 (stretching C=O), 1624 (stretching C=N cm^{-1}), 1604, 1538, 1257. Anal. Calcd. for $C_{64}H_{90}N_2O_8Cu$: C, 71.24; H, 8.41; N, 2.60%. Found: C, 71.51; H, 8.24; N, 2.91%.

RESULTS AND DISCUSSION

Synthesis

The synthetic protocol envisaged the use the 2,4-dihydroxybenzaldehyde as starting reactant, which was treated with the appropriate *n*-alkoxy-benzoic acid and then condensed with 1,12-diaminododecane in a 2:1 molar ratio to give the target compounds **H$_2$L^n** in good yields as summarized in Scheme 1.

The identity of all compounds was confirmed by ^{1}H NMR and IR spectroscopies and elemental analysis. In particular, in the IR spectra of **H$_2$L^n** the C=O band appeared at 1726 cm^{-1}, the C=N band is detected at 1638 cm^{-1} as well as a broad band is observed in the region of the OH stretching. In ^{1}H NMR spectra, recorded in $CDCl_3$ solution, is noticeable the signal attributable to the imminic hydrogen at 8.30 ppm and the phenolic hydrogen signal at 14.13 ppm. Reactions



SCHEME 1 Synthetic route to $\mathbf{H_2L^n}$ ligands.

of the $\mathbf{H_2L^n}$ ligands with an equimolar nickel(II) acetate tetrahydrate or copper(II) acetate monohydrate were carried out in EtOH at reflux, giving rise to the corresponding complexes in good yields. In the IR spectra of the complexes the CN band, with respect to the organic ligand, is shifted to the lower wave numbers upon coordination. On the other hand, the disappearance of the OH absorption confirmed the coordination in an analogous manner such as proposed for similar tetradentate Schiff base ligands with alkyl backbones of eight carbon atoms [15].

Liquid Crystalline Properties

The thermal behaviour of all synthesized species was characterized using both polarized optical microscopy (POM) and differential scanning calorimetry (DSC), while the nature of the mesophase was confirmed using temperature-dependent powder X-ray diffraction (XRD). All thermal data are summarized in Tables 1 and 2.

For both the $\mathbf{H_2L^n}$ ligands, in spite of their *transoid* N,N conformation (Scheme 1), the presence of a very long, flexible alkylene spacer in the core structure, allows the appearance of liquid crystalline character, whatever the length of the terminal substituents grafted on the aromatic rings connected to the salicylaldimine moiety via an ester link. Both ligands, after crystal to crystal transitions,

TABLE 1 Thermal Behaviour of $\mathbf{H_2L^n}$ Ligands

Compound	Transition[a]	T/°C[b]	ΔH/KJ mol^{-1}
$\mathbf{H_2L^1}$	Cr-Cr′	64.7	17.4
	Cr′-N	113.1	43.0
	N-I	133.7	7.7
	I-N	133.1	9.0
	N-Cr	77.8	28.9
$\mathbf{H_2L^2}$	Cr-Cr′	87.2	18.5
	Cr′-Cr″	92.3	38.0
	Cr″-SmC	100.4	15.7
	SmC-N	113.6	1.7
	N-I	121.2	8.3
	I-N	120.9	9.0
	N-SmC	113.8	1.9
	SmC-Cr	80.8	65.2

[a] Cr: crystal; Sm: smectic; N: nematic, I: isotropic liquid.
[b] Temperature data as onset peak.

TABLE 2 Thermal Behaviour of $\mathbf{ML^n}$ Complexes

Compound	Transition[a]	T/°C[b]	ΔH/KJ mol^{-1}
$\mathbf{NiL^1}$	Cr-r′	60.8	4.8
	Cr′-N	239.7	42.3
	N-Idec	264.1	20.7
$\mathbf{NiL^2}$	Cr-Cr′	98.4	13.3
	Cr′-SmC	175.7	30.0
	SmC-N	186.6	0.7
	N- I	195.2	2.8
	I-N	198.3	4.8
	N-SmC + Cr	139.1	31.5
	Cr-Cr′	104.4	12.6
$\mathbf{CuL^1}$	Cr-Cr′	79.4	
	Cr′-SmC	200[c]	2.7
	SmC-N	219[c]	
	N-I dec	232[c]	
$\mathbf{CuL^2}$	Cr-Cr′	92.3	12.7
	Cr′-N	175.5	37.9
	N-I	182.9	1.9
	I-N	176.2	4.2
	N-Cr	144.3	31.5
	Cr-Cr	90.4	12.0

[a] Cr: crystal; Sm: smectic; N: nematic, I: isotropic liquid.
[b] Temperature data as onset peak. [c] Microscopic data.

showed mesomorphism typical of a calamitic material: a nematic phase, with a typical schlieren texture for the lower homologue and a smectic C phase followed by the nematic one, both identified with a schlieren texture, for the higher homologue. As expected, the melting and clearing points as well the temperature range decreased with the elongation of the terminal chains.

After complexation, for all the resulting **ML^n** derivatives, the length-to-breadth ratio does not hamper the molecules to retain a global rod shape and to preserve the calamitic mesomorphism of the corresponding organic precursors, but the mesomorphism has been found to be very sensitive to the metal atom. In particular, the Ni(II) complexes retain the same mesophase sequence of the corresponding organic precursor but the transition temperatures were increased upon complexation. Moreover, comparing the mesomorphic behaviour of **H_2L^1** and the corresponding Ni(II) derivative **NiL^1**, the metal complexation broadens the mesomorphic range even if the relatively high clearing was accompanied by partial decomposition preventing the reproducibility and XRD measurements. With respect to the corresponding ligands, the mesomorphic behaviour is reversed when the Cu(II) replace the Ni(II) centre: indeed the Cu ion promote the appearance and the disappareance of the smectic C phase for the lowest and higher homologues, respectively while the clearing temperatures slightly decrease with respect to the Ni(II) compounds.

The effect of the different metal atoms directly influenced also the thermal stability which, in each series, decreased with increasing the terminal aliphatic chains, but for the highest Cu(II) homologues **CuL^2**, becomes very narrow.

CONCLUSIONS

The aim of the work was to synthesize new paramagnetic metallomesogens for molecule-based devices. Since for this kind of materials the performances strongly depends on the molecular-assembly structures, we have investigated the effect of the variation of single tectons of metal complexes derived from salicylaldimine-based ligands, the most widely used compounds for the synthesis of paramagnetic metallomesogens, on the properties of the overall molecular material.

In particular, a new series of tetradentate Schiff bases with an extended central core has been designed and synthetized by introducing as alkyl spacer a backbone of 12 carbon atoms. Moreover, the influence of the length and position of the peripheral chains has been investigated by introducing two alkoxy substituents (6 or 12 carbon atoms) in the unusual 4 position of the an aromatic rings connected to the salicylaldimine moiety via an ester link.

For both ligands, according to a rod-like overall molecular shape, calamitic mesomorphism is observed, as in similar dimeric salicylaldimine-based mesogens [16] though the alkylene spacer is considerably longer. As usual, increasing the length of the terminal chains, the nematic phase is joined by a smetic C one.

After complexation, even if the archetypal structure of the M(Salen) framework has been deformed and a further variation has been induced through the different nature of the metal ion, the mesomorphism has been retained in the $\mathbf{ML^n}$ derivatives. The introduction of a very long spacer in the central core of the Schiff bases, due to its intrinsic flexibility, did not influence the rod like molecular architecture of the metal complexes, allowing them to retain the global rod-shape of the organic precursors. Moreover, the mutual orientation of the terminal substituents plays an important role in the shape, the molecular assembly and in the induction of liquid crystalline properties. Indeed, nevertheless the length to breath ratio has been modified through complexation, the ribbon-like architecture drives the formation of mesomorphism and, together with the change of the nature of the metal centre, influences only the kind of calamitic phase.

As a whole the mesomorphic properties of the described mesogens evidence that the $\mathbf{H_2L^n}$ ligands, with reference to the corresponding M(II) complexes, reacting with Cu(II) form mesophases at temperature lower that with Ni(II), so suggesting that similar $\mathbf{H_2L^n}$ species featuring a large salicylaldimine spacer can tolerate M(II) ions requiring either a tetrahedral or square planar coordination sphere being, in particular, very useful for the preparation of Cu(II) mesogens. The synthesis of these Cu(II) containing materials with double properties of liquid crystallinity and magnetism allow us to measure their thermomagnetic properties and to find for them proper applications, for example as optically switchable molecular compounds or as dopant in liquid crystalline mixture to improve their orientation properties.

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