



## Synthesis and Mesomorphic Properties of new Metallomesogens derived from azo and Schiff base ligands

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### ABSTRACT

The synthesis, characterization and liquid crystal properties of new seven ligands (L1-L7) and their Cu(II) complexes as well as Ni(II) and VO(IV) for L5. The ligands and their complexes have been characterized by IR, <sup>1</sup>H-NMR, mass spectroscopy and elemental analysis. The liquid crystalline properties of the ligands and the related complexes were studied by differential scanning calorimetry (DSC) and by using a polarizing microscope (POM) equipped with a heating and cooling stage. All the ligands and their complexes exhibit liquid crystalline behavior.

**Keywords:** ligands, Metallomesogens, Cu(II), Ni(II), VO(IV), Thermal stability.

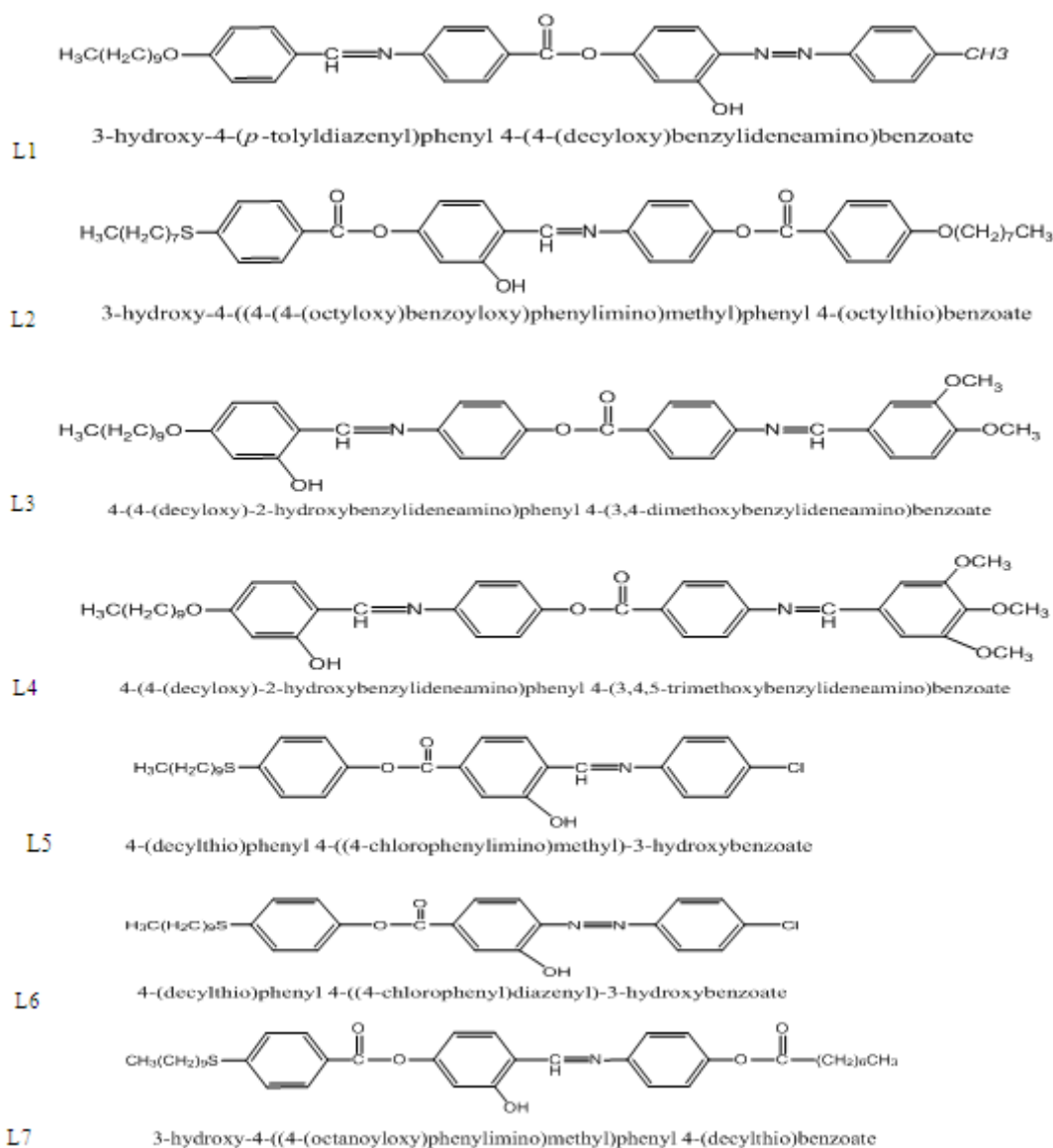
### INTRODUCTION

Metal – containing liquid crystals (Metallomesogens) have received considerable attention recently, due to the ability of the metal to change the liquid crystalline properties of the materials in which it is embedded [1]. The majority of Metallomesogens that have been studied contain d-block metals such as Cu(II), Ni(II), Fe(III) and VO(IV) [1].

Metal complexes of Schiff bases have played an important part in the development of metallomesogens as can be seen from the large number of publications that have appeared in the literature. The particular advantage of the salicyldimine ligand system is the considerable flexibility of synthetic procedure which has allowed the preparation of a wide variety of complexes whose properties are strongly dependent on the ligand structure and on the metal used [2].

On the other hand, Metallomesogens containing complexes azo moieties have been attracting much attention recently due to their possible applications. Due to the clean photochemistry of azobenzene, and substantial change in material properties during light irradiation, it has been investigated as an active component for a variety of applications, such as lithography, non linear optical devices and optical switches [3]. To improve our knowledge of the relationship between metal ion and mesogenic properties, we will analyze in this paper the results of synthetic and mesogenic studies of seven mononuclear Cu(II) complexes Cu(L1)<sub>2</sub>-Cu(L7)<sub>2</sub> derived from new type of Schiff base and azo ligands (fig.1):

Figure.1: Structures of the prepared ligands (L1-L7)



as well as liquid crystalline mononuclear Ni(II) and VO(IV) from L5.

## EXPERIMENTAL SECTION

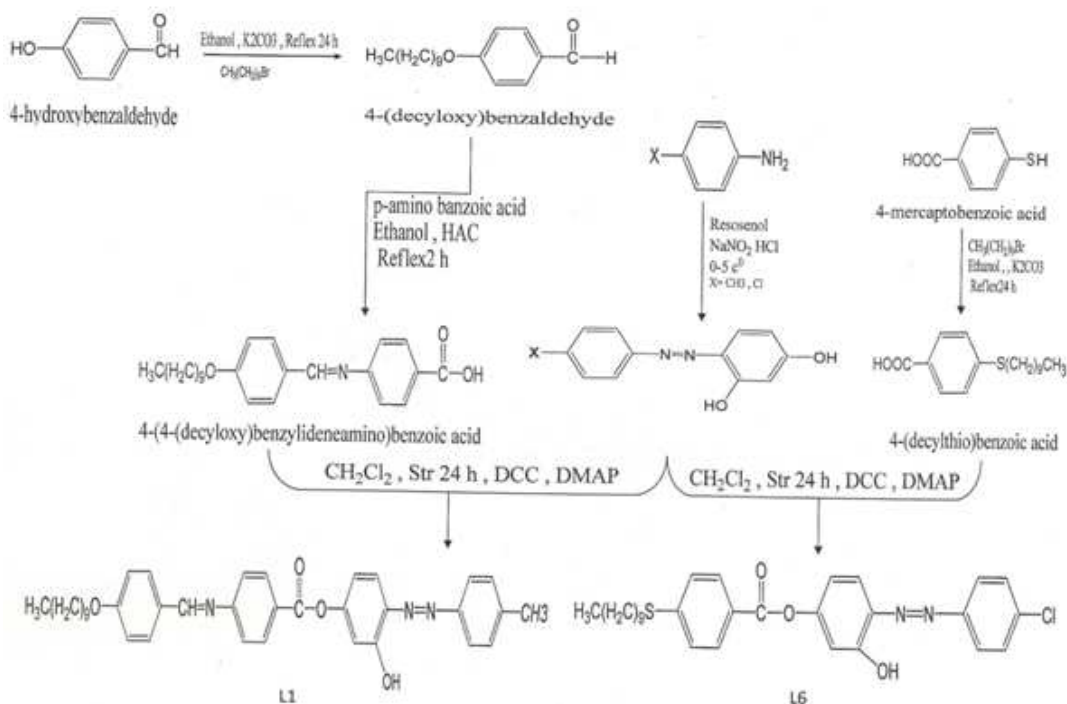
### General

Infrared spectra were recorded as KBr pellets on a Buck – M500 spectrometer.  $^1\text{H-NMR}$  and spectra were recorded on Gemini – 200 using  $\text{CDCl}_3$  as a solvent. Elemental analysis was performed on Euro Vectro EA 3000A. Mass spectra were recorded on Agilent Technologies -5957 C. The phase transitions were observed with a Leitz Laborlux 12 Pol optical microscope with polarized light in conjunction with a leitz 350 hot stage equipped with a Vario – Orthomat camera of transition temperatures were made using a Shimdzu 24 DSC – 50 differential scanning calorimeter with a heating rate of  $10^\circ\text{C min}^{-1}$ .

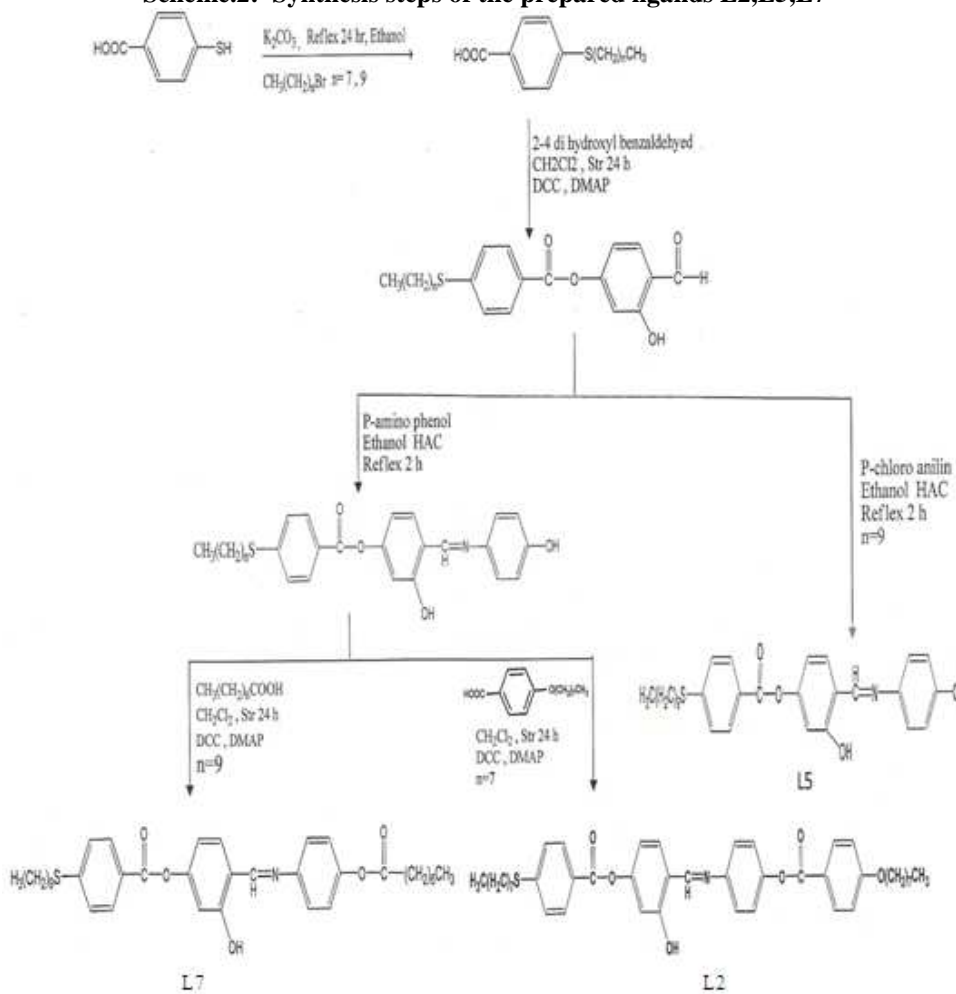
### Synthesis of thioalkyl benzoic acid

Solutions of 4-mercapto benzoic acid (1mmol) in dry ethanol (50ml) and of KOH (2mmol) in dry ethanol (50ml) were magnetically stirred with simultaneous drop-wise addition of 1-octan and decan (1mmol) the reaction mixture was refluxed for 24h and allowed to come to room temperature. The alkoxy potassium salts thus obtained were separated out by filtration under suction and treated with dilute HCl until the pH of the reaction mixture reached ~2. The crude solid white product was filtered off, washed thoroughly with water and recrystallized successively from solution of ethanol [4] scheme 1 and 2.

Scheme.1: Synthesis steps of the prepared ligands L1,L6



Scheme.2: Synthesis steps of the prepared ligands L2,L5,L7

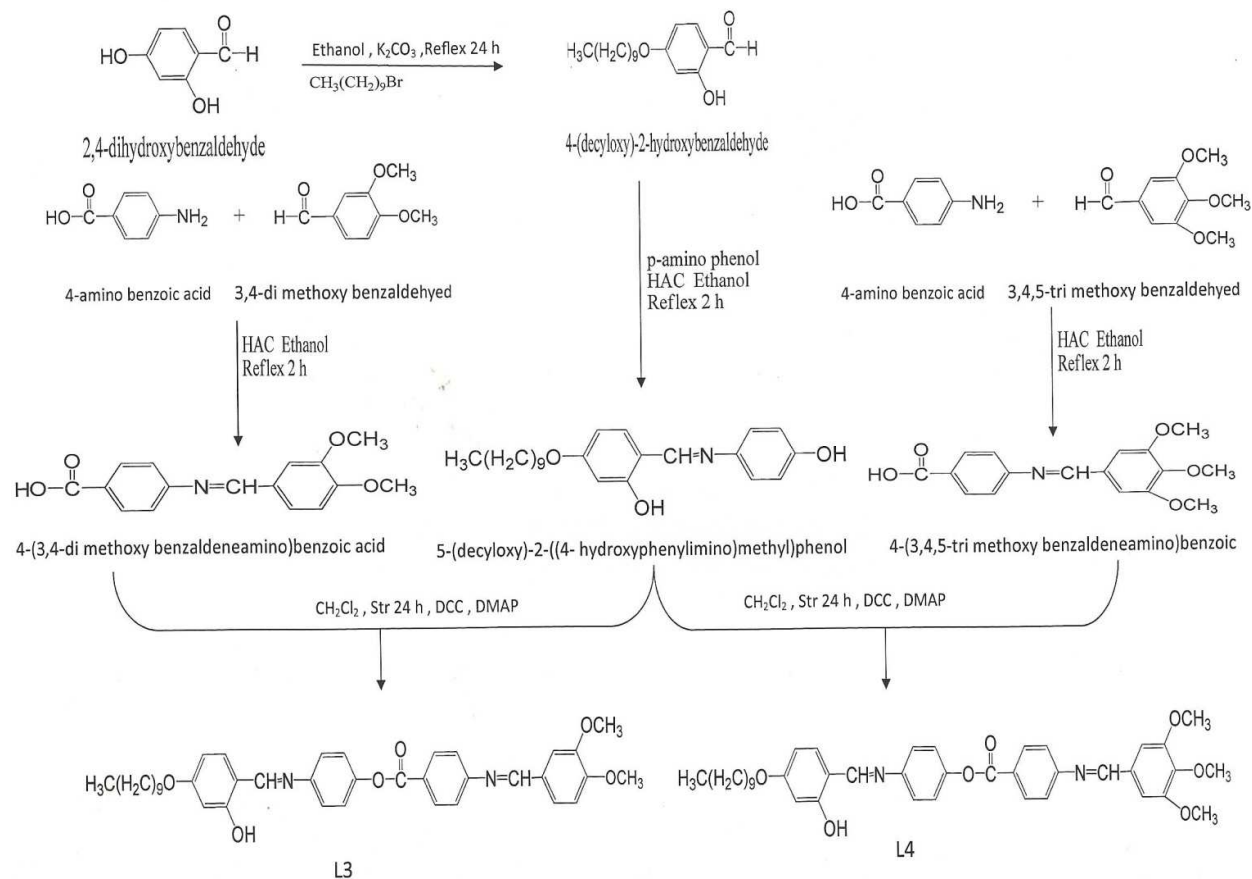


**Synthesis of alkyloxy p-hydroxy and 2,4-dihydroxy benzaldehyde**

4-alkoxy benzaldehydes were prepared by a reported method [5,6], (scheme 1 and 3).

**Synthesis of esters**

Esters were synthesized by a modification of a literature method [7], (scheme 1,2 and 3).

**Scheme.3: Synthesis steps of the prepared ligands L3,L4****Synthesis of azo**

Azo were synthesized by a modification of a literature method [8], (scheme 1).

**Synthesis of Schiff bases**

Absolute ethanolic solutions of appropriate amine for the prepared compounds (10 mmol) and appropriate ester (10 mmol) were stirred for 2h in presence of a few drops of acetic acid and the resultant solution was left at room temperature [9]. The micro-crystalline yellow colored product, was suction-filtered, thoroughly washed with ethanol, recrystallized from hexane (scheme 1,2 and 3).

**Synthesis of Complexes**

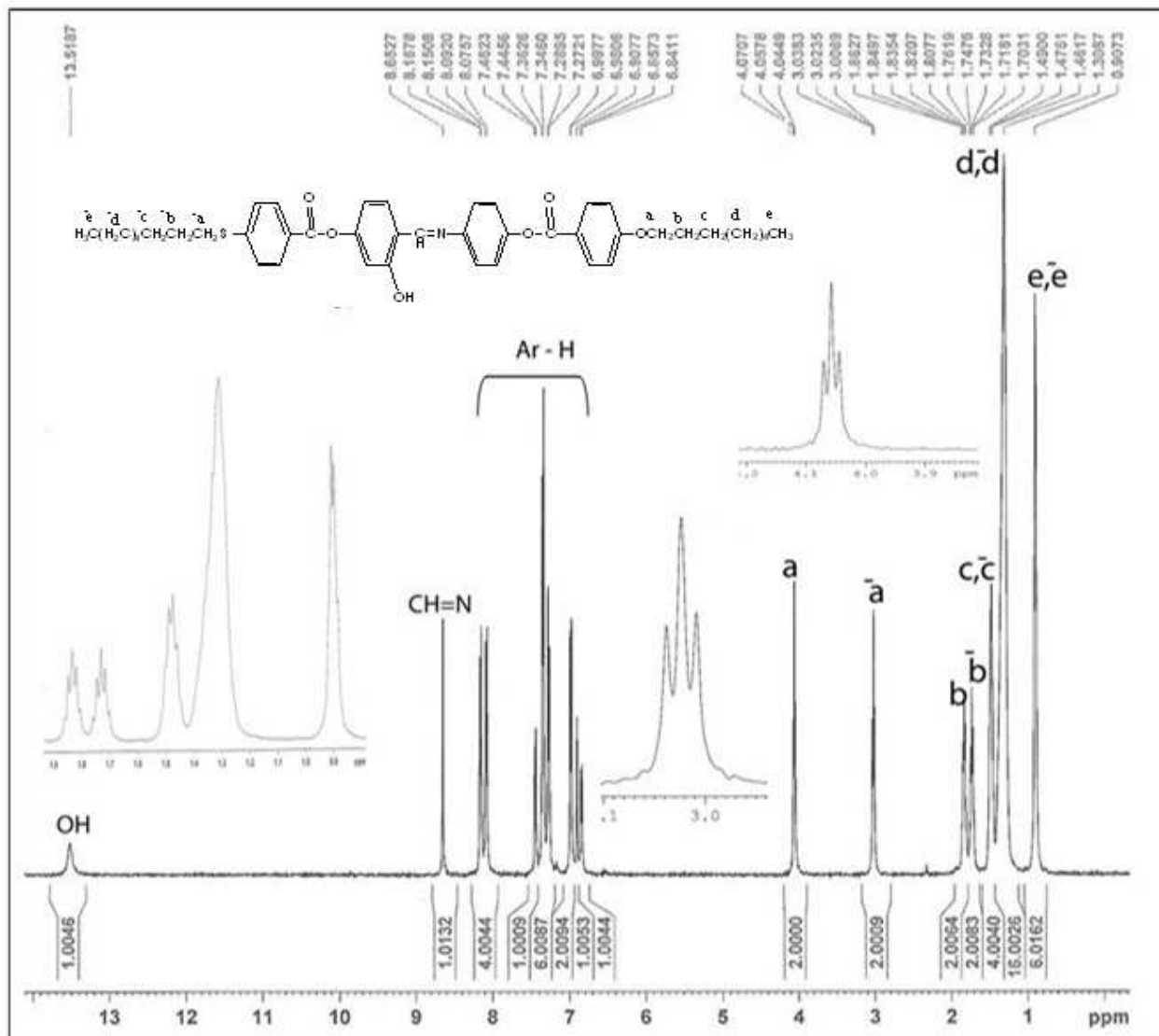
All the complexes were prepared from the corresponding metal salt Copper (II) acetate, Oxovanadium (IV) sulfate, and nickel (II) acetate: an ethanolic solution containing the metal salt (1 mmol) was added to a hot ethanolic solution of the ligand (2mmol). The solution was refluxed for 2 hr. and then cooled. The precipitate was filtered and recrystallized in chloroform [10,11]

3-hydroxy-4-(p-tolyldiazenyl)phenyl 4-(4-(decyloxy)benzoyloxy)phenylimino)benzoate (L1): Orange solid; yield 42.4%;  $^1\text{H-NMR}$   $\delta$  0.905(t, 3H,  $\text{CH}_3$ ), 1.262 – 1.486 (m, 12H,  $(\text{CH}_2)_6$ ), 1.514(qui, 2H,  $\text{CH}_2$ ), 1.892(qui, 2H,  $\text{CH}_2$ ), 2.399(s, 3H,  $\text{CH}_3$ ), 4.047(t, 2H,  $\text{OCH}_2$ ), 6.514 – 8.239 (m, 15H, Ar-H), 8.394(s, 1H,  $\text{CH}=\text{N}$ ), 13.308(s, 1H, OH); IR ( $\text{cm}^{-1}$ ) [12-14]: 1720 (C=O), 1618 (C=N); MS m/z (%): 591.3 [M] $^+$ .

3-Hydroxy-4-((4-(4-(octyloxy)benzoyloxy)phenylimino)methyl)phenyl 4-(octylthio) benzoate (L2): White solid; yield 66.8%;  $^1\text{H-NMR}$   $\delta$  0.907(t, 6H,  $(\text{CH}_3)_2$ ), 1.308(m, 16H,  $(\text{CH}_2)_8$ ), 1.476(qui, 4H,  $(\text{CH}_2)_6$ ), 1.732(qui,

2H , CH<sub>2</sub>) , 1.834(qui , 2H , CH<sub>2</sub>) , 3.025 (t , 2H , SCH<sub>2</sub>) , 4.057(t , 2H , OCH<sub>2</sub>) , 6.841 – 8.167(m , 15H , Ar-H) , 8.652(S , 1H , CH=N) 13.518(S , 1H , OH) ; IR (cm<sup>-1</sup>) : 1724 (C=O), 1614 (C=N) ; MS m/z (%) : 708.7 [M]<sup>+</sup> .

Figure 5: <sup>1</sup>H-NMR and the expansion for aliphatic protons of L<sub>2</sub>



4-(4-(decyloxy)-2-hydroxybenzylideneamino)phenyl 4-(3,4-dimethoxy benzylideneamino) benzoate (L3): Yellow solid; yield 90.4%;  $^1\text{H-NMR}$   $\square\square$  0.905(t, 3H,  $\text{CH}_3$ ), 1.286- 1.364(m, 12H,  $(\text{CH}_2)_6$ ), 1.484(qui, 2H,  $\text{CH}_2$ ), 1.807(qui, 2H,  $\text{CH}_2$ ), 3.989(s, 6H,  $(\text{CH}_3)_2$ ), 4.018(t, 2H,  $\text{OCH}_2$ ), 6.448-8.253 (m, 14H, Ar-H), 8.384(S, 1H,  $\text{CH}=\text{N}$ ), 8.548(S, 1H,  $\text{CH}=\text{N}$ ), 13.638 (S, 1H, OH); IR ( $\text{cm}^{-1}$ ): 1726 (C=O), 1620 (C=N); MS m/z (%): 636.8  $[\text{M}]^+$ .

4-(4-(decyloxy)-2-hydroxybenzylideneamino)phenyl 4-(3,4,5-trimethoxy benzylideneamino) benzoate (L4): Yellow solid; yield 88.25%;  $^1\text{H-NMR}$   $\square\square$  0.895(t, 3H,  $\text{CH}_3$ ), 1.289- 1.380(m, 12H,  $(\text{CH}_2)_6$ ), 1.467(qui, 2H,  $\text{CH}_2$ ), 1.807(qui, 2H,  $\text{CH}_2$ ), 3.988(S, 9H,  $(\text{CH}_3)_3$ ), 4.017(t, 2H,  $\text{OCH}_2$ ), 6.448-8.253 (m, 14H, Ar-H), 8.384(S, 1H,  $\text{CH}=\text{N}$ ), 8.547(S, 1H,  $\text{CH}=\text{N}$ ), 13.638 (S, 1H, OH); IR ( $\text{cm}^{-1}$ ): 1733 (C=O), 1623 (C=N); MS m/z (%): 656.7  $[\text{M}]^+$ .

4-((4-chlorophenylimino) methyl)-3-hydroxyphenyl 4-(decylthio) benzoate (L5): yellow solid; yield 75.3%;  $^1\text{H-NMR}$   $\square\square$  0.892(t, 3H,  $\text{CH}_3$ ), 1.290 – 1.323(m, 12H,  $(\text{CH}_2)_6$ ), 1.488(qui, 2H,  $\text{CH}_2$ ), 1.730(qui, 2H,  $\text{CH}_2$ ), 3.021(t, 2H,  $\text{SCH}_2$ ), 6.834 – 8.084(m, 11H, Ar-H), 8.164(S, 1H,  $\text{CH}=\text{N}$ ), 13.362(S, 1H, OH); IR ( $\text{cm}^{-1}$ ): 1730 (C=O), 1618 (C=N); MS m/z (%): 523.3  $[\text{M}]^+$ .

4-((4-chlorophenyl)diazenyl)-3-hydroxyphenyl 4-(decylthio) benzoate (L6): Orange solid; yield 75.8%;  $^1\text{H-NMR}$   $\square\square$  0.905 (t, 3H,  $\text{CH}_3$ ), 1.280 – 1.323(m, 12H,  $(\text{CH}_2)_6$ ), 1.493(qui, 2H,  $\text{CH}_2$ ), 1.732(qui, 2H,  $\text{CH}_2$ ), 3.025 (t, 2H,  $\text{SCH}_2$ ), 6.922 – 8.089(m, 11H, Ar-H), 13.041(S, 1H, OH); IR ( $\text{cm}^{-1}$ ): 1732 (C=O); MS m/z (%): 524.3  $[\text{M}]^+$ .

3-hydroxy-4-((4-octanoyloxy) phenylimino)methyl) phenyl 4-(decylthio) benzoate (L7): yellow solid; yield 73.56.3%;  $^1\text{H-NMR}$   $\square\square$  0.893(t, 6H,  $(\text{CH}_3)_2$ ), 1.290 – 1.323(m, 20H,  $(\text{CH}_2)_{10}$ ), 1.359(qui, 2H,  $\text{CH}_2$ ), 1.723(qui, 2H,  $\text{CH}_2$ ), 1.738(qui, 2H,  $\text{CH}_2$ ), 2.575(t, 2H,  $\text{CH}_2$ ), 3.013 (t, 2H,  $\text{CH}_2$ ), 6.828 – 8.616(m, 11H, Ar-H), 8.649(S, 1H,  $\text{CH}=\text{N}$ ), 13.463(S, 1H, OH); IR ( $\text{cm}^{-1}$ ): 1735 (C=O), 1622 (C=N); MS m/z (%): 630.8  $[\text{M}]^+$ .

bis(5-(4-(4-(decyloxy)benzylideneamino)benzoyloxy)-2-(p-tolyldiazenyl)phenoxy)copper  $\text{Cu}(\text{L1})_2$ ): Brown solid; yield 66.42%; IR ( $\text{cm}^{-1}$ ): 1726 (C=O), 1602 (C=N); elemental analysis calc. for  $\text{C}_{74}\text{H}_{80}\text{N}_6\text{O}_8\text{Cu}$ : %C 71.38, %H 6.43, %N 6.75 found 71.38, %H 6.43, %N 6.75 C 71.36, %H 6.51, %N 6.70.

(5-(2-Hydroxy-4-(octylthio)benzoyloxy)-2-((4-(4-(octyloxy)benzoyloxy) phenylimino)methyl) phenoxy) (2-((4-(4-(octyloxy)benzoyloxy)phenylimino)methyl)-5-(4-(octylthio) benzoyloxy)phenoxy) copper  $\text{Cu}(\text{L2})_2$ : green solid; yield 73.08%; IR ( $\text{cm}^{-1}$ ): 1726 (C=O), 1606 (C=N); elemental analysis calc. for  $\text{C}_{86}\text{H}_{100}\text{N}_2\text{O}_{12}\text{S}_4\text{Cu}$ : %C 69.72, %H 6.75, %N 1.89, %S 8.64 found C 69.67, %H 6.71, %N 1.78, %S 8.43.

bis(5-(decyloxy)-2-((4-(4-(3,4-dimethoxy benzylideneamino) benzoyloxy) phenyl amino)methyl) phenoxy) copper  $\text{Cu}(\text{L3})_2$ ): Brown solid; yield 80.13%; IR ( $\text{cm}^{-1}$ ): 1724 (C=O), 1612 (C=N); elemental analysis calc. for  $\text{C}_{78}\text{H}_{86}\text{N}_4\text{O}_{12}\text{Cu}$ : %C 70.16, %H 6.44, %N 4.19 found C 70.09, %H 6.35, %N 4.08.

bis(5-(decyloxy)-2-((4-(4-(3,4,5-trimethoxy benzylideneamino) benzoyloxy) phenyl amino)methyl) phenoxy) copper  $\text{Cu}(\text{L4})_2$ : green solid; yield 76.93%; IR ( $\text{cm}^{-1}$ ): 1720 (C=O), 1610 (C=N); elemental analysis calc. for  $\text{C}_{80}\text{H}_{90}\text{N}_4\text{O}_{14}\text{Cu}$ : %C 68.86, %H 6.44, %N 4.01 found C 68.67, %H 6.36, %N 3.88.

bis(2-((4-chlorophenylimino) methyl)-5-(4-decylthio) benzoyloxy)phenoxy)copper  $\text{Cu}(\text{L5})_2$ : Brown solid; yield 74.36%; IR ( $\text{cm}^{-1}$ ): 1728 (C=O), 1606 (C=N); elemental analysis calc. for  $\text{C}_{60}\text{H}_{66}\text{N}_2\text{O}_6\text{S}_2\text{Cl}_2\text{Cu}$ : %C 64.98, %H 5.95, %N 2.52, %S 5.77 found C 64.75, %H 5.78, %N 2.33, %S 5.38.

bis(2-((4-chlorophenylimino) methyl)-5-(4-decylthio) benzoyloxy)phenoxy)nickel  $\text{Ni}(\text{L5})_2$ : green solid; yield 78.55%; IR ( $\text{cm}^{-1}$ ): 1720 (C=O), 1613 (C=N); elemental analysis calc. for  $\text{C}_{60}\text{H}_{66}\text{N}_2\text{O}_6\text{S}_2\text{Cl}_2\text{Ni}$ : %C 65.27, %H 5.98, %N 2.53, %S 5.80 found C 65.03, %H 5.64, %N 2.14, %S 5.66.

bis(2-((4-chlorophenylimino) methyl)-5-(4-decylthio) benzoyloxy)phenoxy)vanadium  $\text{VO}(\text{L5})_2$ : Brown solid; yield 76.11%; IR ( $\text{cm}^{-1}$ ): 1728 (C=O), 1602 (C=N); elemental analysis calc. for  $\text{C}_{60}\text{H}_{66}\text{N}_2\text{O}_7\text{S}_2\text{Cl}_2\text{VO}$ : %C 64.80, %H 5.94, %N 2.52, %S 5.76 found C 64.55, %H 5.73, %N 2.23, %S 5.38.

bis(2-((4-chlorophenyl)diazenyl)-5-(4-(decylthio) benzoyloxy)phenoxy) copper  $\text{Cu}(\text{L6})_2$ ): Brown solid; yield 89.53%; IR ( $\text{cm}^{-1}$ ): 1731 (C=O); elemental analysis calc. for  $\text{C}_{58}\text{H}_{64}\text{N}_4\text{O}_6\text{S}_2\text{Cl}_2\text{Cu}$ : %C 62.70, %H 5.76, %N 5.04, %S 5.76 found C 62.48, %H 5.53, %N 4.89, %S 5.33.

bis(2-((4-chlorophenyl)diazenyl)-5-(4-(decylthio) benzyoxy)phenoxy) copper Cu(L7)2 ): Brown solid; yield 89.53%; IR (cm<sup>-1</sup>) : 1725 (C=O), 1602 (C=N) ;elemental analysis calc.for C<sub>76</sub>H<sub>96</sub>N<sub>2</sub>O<sub>10</sub>S<sub>2</sub>Cu:%C 73.56,%H 7.25,%N 2.11, %S 4.83 found C 73.33,%H 7.01,%N 1.87, %S4.46.

### RESULTS AND DISCUSSION

The phase transition temperatures of ligands and their complexes obtained from DSC analysis and polarized optical microscopy are tabulated in Table 1, 2 and 3.

All the ligands synthesized exhibit liquid crystal properties , the mesophases exhibited by the ligands were identified as Smectic (Sc) in L1,L2,L5,L6 and L7 but Nematic phase (N) in L3 and L4 (table.1).

**Table 1. Thermal and thermodynamic data for ligands**

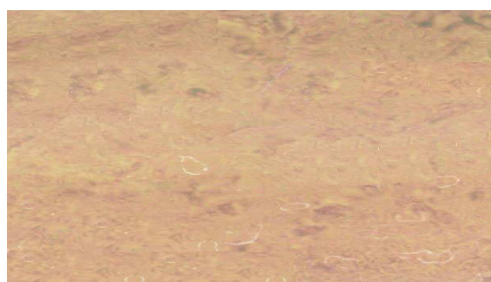
Compounds	Phase Transition Temperatures °C	ΔH j/g	ΔT <sub>S</sub>	ΔT <sub>N</sub>
L1	C-S	128.82	59.29	151.81
	S-I	280.63	6.04	
L2	C-S	136.69	59.96	123.43
	S-I	260.12	5.05	
L3	C-N	123.31	56.32	-
	N-I	241.91	4.28	
L4	C-N	121.76	59.54	-
	N-I	232.58	4.05	
L5	C-S	89.94	64.92	94.18
	S-I	184.12	6.59	
L6	C-S	104.83	99.61	104.74
	S-I	209.57	7.37	
L7	C-S	98.46	66.54	81.54
	S-I	180.00	4.22	

The mesophases were identified by their textures observed by optical microscopy a marbled texture in the heating process and a schlieren texture on cooling allowed as to identify the Nematic phase .The Smectic (Sc) exhibits Schlieren texture on heating and cooling . The mesophases exhibited by the complexes were also identified as Smectic (Sc) and Nematic (N) by their optical textures , which are similar to those observed for ligands .A photomicrograph of the mesophases phases can be seen in figure 2.

**Figure 2. a: Schlieren texture of the smectic (Sc) in heating of L6, b: Marble texture for Nematic phase in heating for L3, C: Schlieren texture for Nematic phase in cooling for L3 .**



a



b



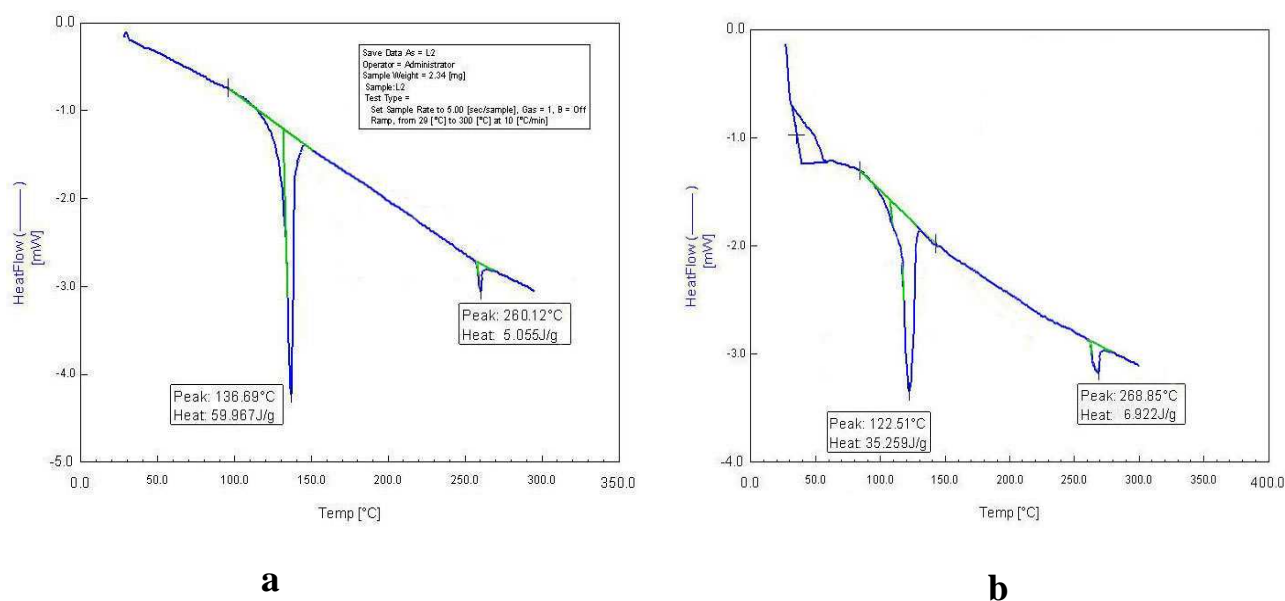
928  
c

We observed that most of the complexes partially decompose after the complex has become isotropic and the second DSC scan shows the transition at lower temperatures. For this reason first-scan DSC data were used. The complexes melt at higher temperatures than the ligands. The mesophases ranges of the Cu(II) complexes are considerably wider than the ligands (table 2 and figure 2).

**Table 2. Thermal and thermodynamic data for complexes**

Compounds	Phase Transition Temperatures <sup>0</sup> C	$\Delta H$ j/g	$\Delta T_S$	$\Delta T_N$
<b>Cu(L1)<sub>2</sub></b>	C-S	121.56	50.05	171.35
	S-I	292.91	4.46	
<b>Cu(L2)<sub>2</sub></b>	C-S	122.51	35.25	166.34
	S-I	288.85	6.92	
<b>Cu(L3)<sub>2</sub></b>	C-N	131.26	28.37	-
	N-I	278.45	4.23	
<b>Cu(L4)<sub>2</sub></b>	C-N	130.30	35.25	-
	N-I	268.41	4.22	
<b>Cu(L5)<sub>2</sub></b>	C-S	132.83	95.61	127.50
	S-I	260.33	6.13	
<b>Cu(L6)<sub>2</sub></b>	C-S	123.94	79.91	146.30
	S-I	270.24	6.27	
<b>Cu(L7)<sub>2</sub></b>	C-S	107.26	28.77	114.19
	S-I	221.45	6.98	

**Figure 3: DSC thermogram for a. L2, b. Cu(L2)<sub>2</sub>**

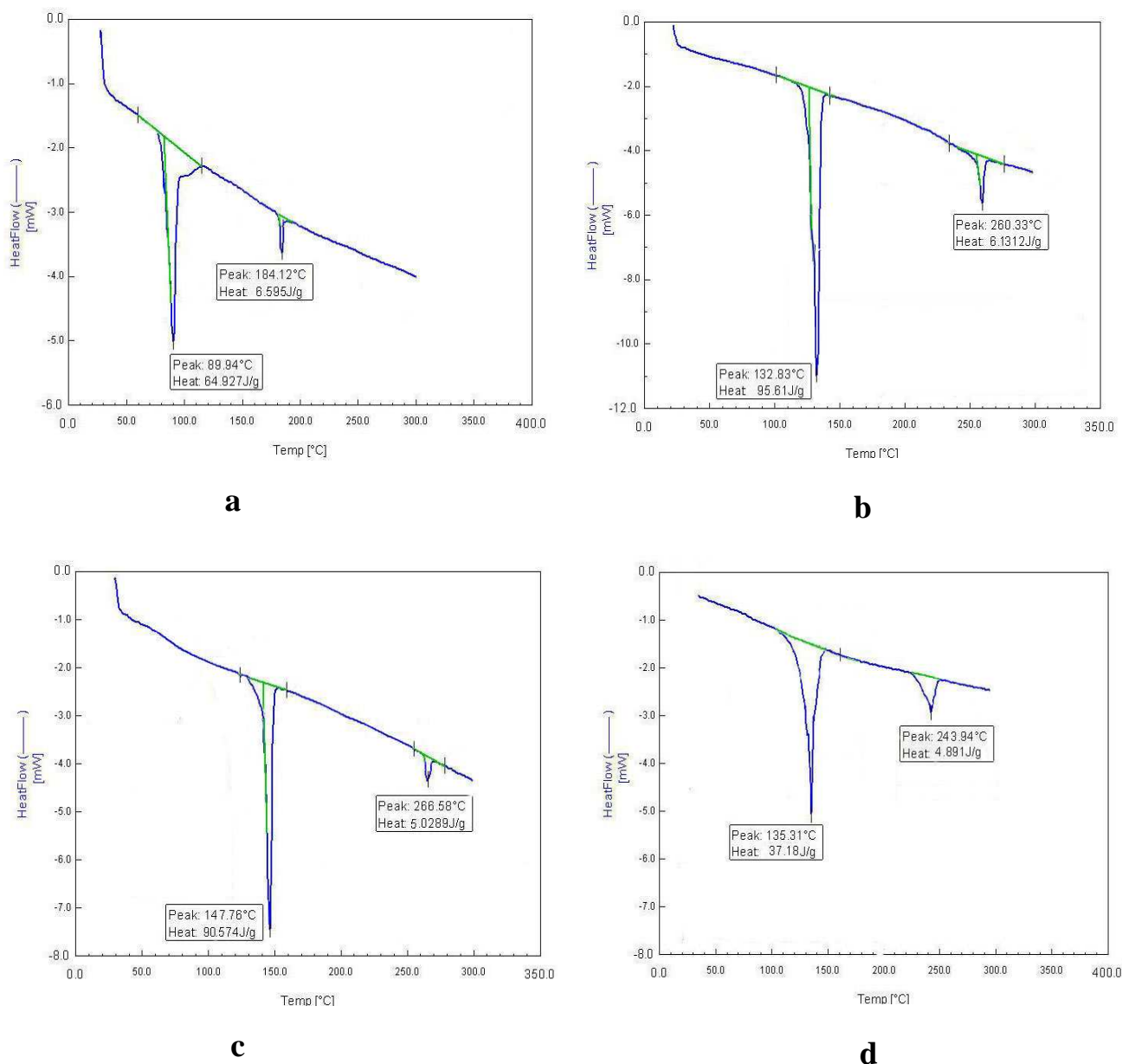


Comparative study of the Cu(L5)<sub>2</sub>, Ni(L5)<sub>2</sub> and VO(L5)<sub>2</sub> (table.3 and figure 4 ) allow us to draw some interesting conclusions .The copper (II) complexes exhibit larger mesogenic ranges than the other two analogue. Normally the mesogenic range decreases in the order Cu > Ni > VO . An explanation of this phenomenon can be obtained based on the geometries of the complexes .



Table 3. Thermal and thermodynamic data for L5 and complexes

Compound	Phase Transition Temperatures °C	$\Delta H$ J/g	$\Delta T_s$
L5	C-S	89.94	64.92
	S-I	184.12	6.59
Cu(L5) <sub>2</sub>	C-S	132.83	95.61
	S-I	260.33	6.13
Ni(L5) <sub>2</sub>	C-S	147.76	90.57
	S-I	266.58	5.02
VO(L5) <sub>2</sub>	C-S	135.31	37.18
	S-I	243.94	4.89

Figure 4: DSC thermogram for a. L5, b. Cu(L5)<sub>2</sub>, c. Ni(L5)<sub>2</sub>, d. VO(L5)<sub>2</sub>

The Copper (II) and Ni (II) have a square – planar geometry which is susceptible to tetrahedral distortion . The Oxovanadium (IV) complexes have a square – pyramidal geometry .

The square planar geometry of the copper (II) complexes in the mesomorphic state allows a better molecular packing arrangement than in the other metal complexes, favoring the appearance of more ordered mesophases. Consequently, the copper (II) complexes are better smectogenic than the other complexes [15-18].

#### CONCLUSION

New Cu(II) Metallomesogens of Schiff base and azo Ligands have been synthesized. All Ligands and Cu(II) Metallomesogens exhibit Liquid crystalline properties. The mesophases range in the Cu(II) complexes wider than Ligands. The mesophases range in the Cu(II), Ni(II) and VO(IV) complexes of L5 decrease in the order Cu > Ni > VO.

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