

## Columnar phases exhibited by some polycatenar ligands and a few related metal complexes

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**Abstract.** The synthesis and characterization of some polycatenar ligands which exhibit hexagonal columnar and cubic phases are reported. A pentacatenar with only four phenyl rings in the core and exhibiting a mesophase is also reported. A few copper (II) and palladium (II) complexes have been synthesized using these ligands and the mesomorphic properties exhibited by them are described. The hexagonal columnar phase exhibited by some of the complexes can be cooled down to room temperature. The mesophases have been characterized using a combination of polarized light microscopy, differential scanning calorimetry and X-ray diffraction methods.

**Keywords.** Columnar phase; cubic phase; polycatenar; metal complex.

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### 1. Introduction

It is twenty-five years since the discovery of the columnar phase [1] in compounds composed of disc-like molecules. There has been remarkable progress during this long period of time and several review articles have been written on the subject [2–5]. The phasmids and in general, the polycatenar compounds [6] form a different class of materials which also exhibit the columnar phase, though the organization of molecules in the columns is different. The polycatenar mesogens, particularly the penta- and tetra-catenars show very rich polymesomorphism. One of the most interesting features of these is that they show smectic, cubic and columnar phases in many of the pure individual compounds. Based on the investigations carried out on a large variety of compounds [6], several generalizations have been made regarding the occurrence of mesophases. These include the number of rings required in the core, the type and number of terminal chains, the nature of the bridging groups etc.

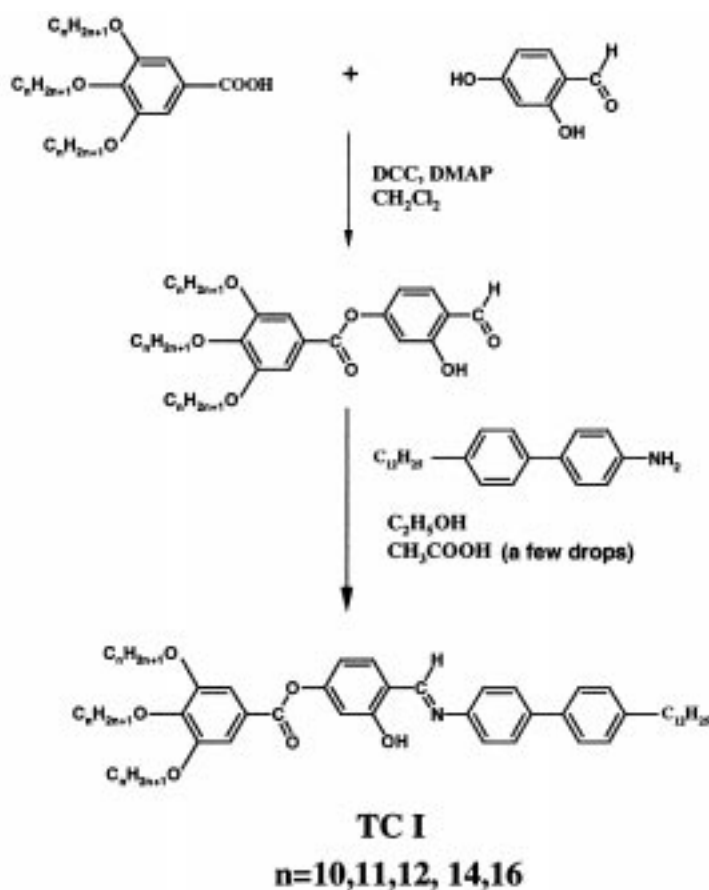
Metallomesogens [7] form another class of materials, most of them coloured, and are fairly high melting. One of the attractive features of metallomesogens is that molecular shapes not accessible in pure organic compounds, can be achieved rather easily. Both rod-like and disc-like metallomesogens have been made and all the principal mesophase types have been observed. Many thermotropic metallomesogens have been prepared by incorporating different metals, including representatives of s-, p-, d- and even f-block elements.

The aim of the present investigation was to prepare suitable polycatenar ligands and use them for synthesizing metal complexes. To the best of our knowledge, there is only

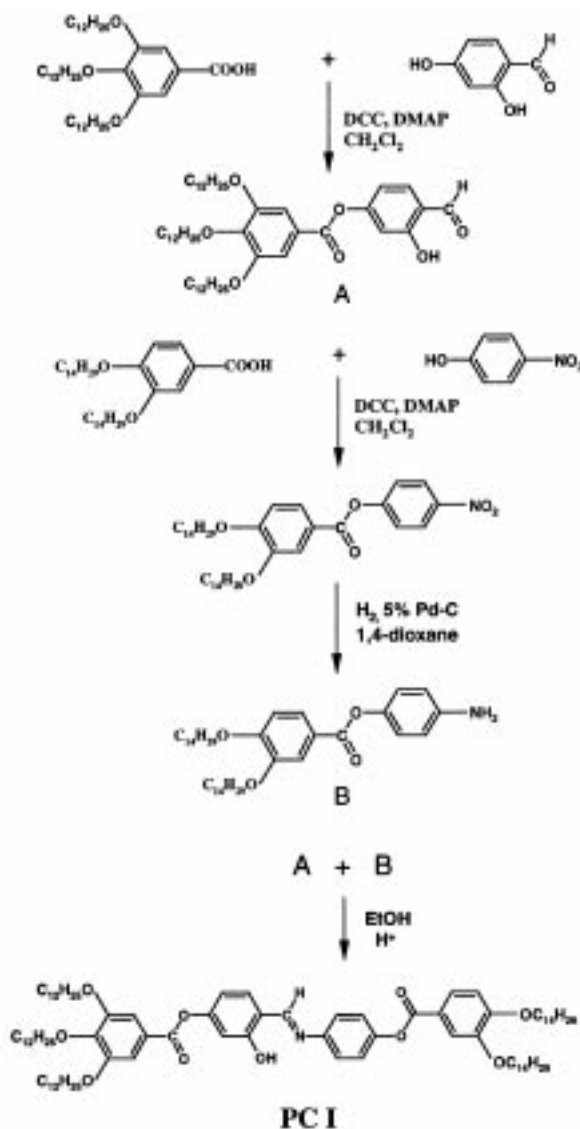
one copper (II) complex of a tetracatenar mesogen [6] reported so far exhibiting a columnar phase and the transition temperatures are very high. Recently, hexacatenar chiral oxazoline complexes have been reported [8] and mesomorphic properties were not observed in neat materials. In this paper, we present the mesomorphic properties of some tetra- and pentacatenar ligands and a few of their copper (II) and palladium (II) complexes.

## 2. Experimental

The tetracatenar ligands containing four phenyl rings were prepared following the synthetic pathway shown in scheme 1. 3,4,5-Tri-*n*-alkoxybenzoic acids were prepared by alkylating methyl gallate using appropriate *n*-alkyl bromides in the presence of anhydrous potassium carbonate, followed by hydrolysis of the resulting ester. Resorcyaldehyde was prepared following a well-known procedure [9]. 4-Amino 4-*n*-alkylbiphenyl was prepared following a procedure described by us [10]. The tetracatenar ligands containing only three phenyl rings were synthesized following the same route shown in scheme 1,



**Scheme 1.** Synthetic pathway used for the preparation of tetracatenar compounds, TCI.



**Scheme 2.** Synthetic pathway used for the preparation of pentacatenar ligand, **PC I**.

except that instead of 4-amino 4-*n*-alkylbiphenyl, 4-*n*-tetradecyloxyaniline was used. 4-*n*-Tetradecyloxyaniline was prepared following standard procedures [11]. The pentacatenar ligands containing four phenyl rings were prepared following a route shown in scheme 2. 3,4-Di-*n*-tetradecyloxy benzoic acid was prepared from ethyl 3,4-dihydroxybenzoate. The copper (II) and palladium (II) complexes were prepared following procedures similar to those already described [12]. All the compounds were purified by column chromatography and repeated crystallization from suitable solvents and characterized using spectroscopic

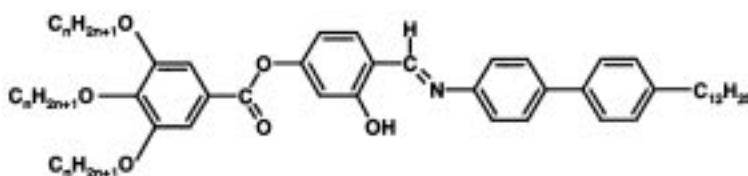
methods and elemental analysis. The detailed experimental procedures and analytical data will be reported elsewhere. The mesomorphic behaviour of all the materials was examined by using a polarized light microscope (Leitz Laborlux 12 POL/Olympus BX50) equipped with a heating stage and controller (Mettler FP52 and FP5 respectively) and also from thermograms recorded on a differential scanning calorimeter (DSC, Perkin-Elmer, Model Pyris ID). X-ray diffraction studies were carried out using Cu-K $\alpha$  radiation from a rotating anode generator (Rigaku Ultrax 18) with a flat graphite crystal monochromator. The diffraction patterns were collected on an image plate (Marresearch). Unoriented samples were taken in Lindemann capillaries and the sample temperature was controlled to within  $\pm 0.1^\circ\text{C}$ .

### 3. Results and discussion

#### 3.1 Tetracatenar compounds and their metal complexes

In order to avoid any confusion and to maintain uniformity, we have used the same notation for identifying the position of the terminal chains with respect to the bridging group that was proposed in the original work [6]. Thus, the tetracatenar compounds under investigation can be called a  $3(mpm)-1(p)$  system. The transition temperatures of the five tetracatenar compounds, **TC I**, containing four aromatic rings in the core including a biphenyl moiety are summarized in table 1. All the five compounds are enantiotropic mesomorphic and show interesting behaviour. On melting the crystals of compound **1**, only dark regions could be seen and it was difficult to detect the clearing temperature under a polarizing microscope. However, this transition could be clearly seen on a DSC thermogram. The clearing enthalpy determined was of the order of  $2.47\text{ kJ mol}^{-1}$ . Compound **2** melts to a birefringent phase when observed between two glass plates under a polarizing microscope. On slow cooling of the isotropic liquid, very colourful spherulites could be seen to grow and a photomicrograph of this is shown in figure 1. These spherulites coalesce on lowering the temperature and the texture looks similar to those observed for a columnar phase. On decreasing the temperature further to  $70^\circ\text{C}$ , dark regions start appearing and the whole field of view becomes dark. The birefringent columnar phase could be obtained by heating

**Table 1.** Transition temperatures ( $^\circ\text{C}$ ) for the series of compounds, **TC I**.



Compound	$n$	Cr	Cub	Col <sub>hd</sub>	I			
<b>1</b>	10	·	67.0	·	83.5	-	·	
<b>2</b>	11	·	73.5	(·	70.0)	·	80.5	·
<b>3</b>	12	·	70.0	·	77.0	·	80.5	·
<b>4</b>	14	·	74.0	(·	64.0)	·	79.5	·
<b>5</b>	16	·	71.5	-	-	·	76.0	·

this dark phase. This dark phase has been identified to be a cubic phase in analogy with what is observed for tetracatenar mesogens [6], and we have not yet investigated this phase further. Similar behaviour was observed for compounds **3** and **4** as well. A photomicrograph showing the columnar phase developing from the isotropic liquid of compound **3** is shown in figure 2 while in figure 3, the cubic phase growing from the columnar phase can be seen. However, on increasing the chain length to *n*-hexadecyloxy (compound **5**), the cubic phase gets eliminated and only the columnar phase is retained.



**Figure 1.** Optical photomicrograph of the hexagonal columnar phase developing from the isotropic liquid, compound **2**, 79.0°C.



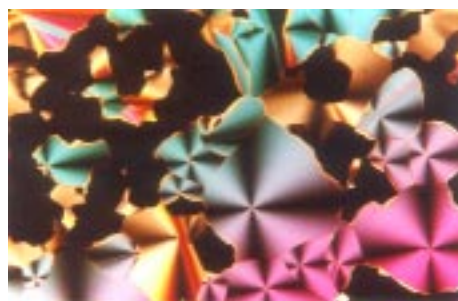
**Figure 2.** Optical photomicrograph of the hexagonal columnar phase developing from the isotropic liquid, compound **3**, 79.5°C.



(a)

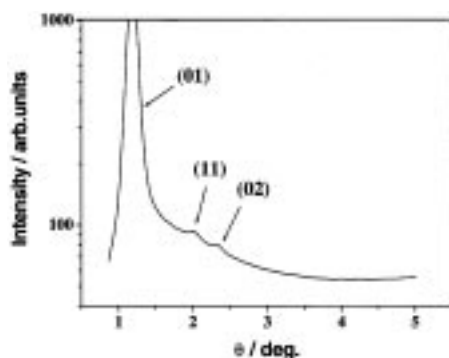


(b)



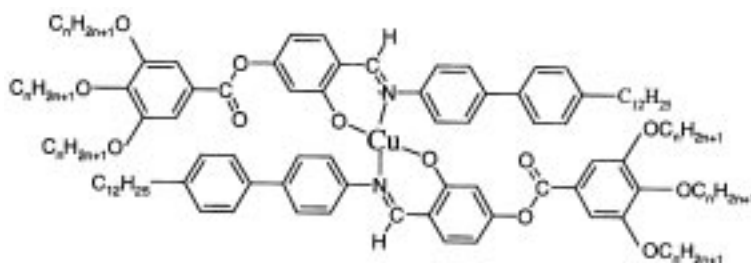
(c)

**Figure 3.** Optical photomicrographs showing (a) the hexagonal columnar disordered phase, (b) the cubic phase developing from the hexagonal columnar phase and (c) the cubic phase in large domains, compound **4**, 63.5°C.



**Figure 4.** X-ray angular intensity profile obtained in the hexagonal columnar phase of compound **3**, at 78°C.

**Table 2.** Transition temperatures (°C) for the series of copper complexes, **TC I Cu**.



Compound	<i>n</i>	Cr	Col <sub>hd</sub>	I
<b>6</b>	10	·	89.0	-
<b>7</b>	11	·	92.0	(· 83.0)
<b>8</b>	12	·	74.0	· 95.5
<b>9</b>	14	·	72.5	· 95.0
<b>10</b>	16	·	73.0	· 98.0

In order to investigate the birefringent mesophase in detail, X-ray diffraction experiments were carried out on unoriented samples. For example, for compound **3**, the X-ray diffraction patterns exhibit the characteristic feature of a hexagonal columnar structure. In other words, three reflections were obtained in the small-angle region, with their spacings in the ratio  $1 : 1/\sqrt{3} : 1/2$ . They can be indexed as the (01), (11), and (02) reflections from a two-dimensional hexagonal lattice, with the lattice parameter  $a = 43.1 \text{ \AA}$ . In addition, a wide-angle diffuse peak was obtained at about  $4.5 \text{ \AA}$ , indicating fluidity of the alkyl chains. The angular X-ray intensity profile obtained for this compound is shown in figure 4. This supports the observations made under the polarized light optical microscope that the mesophase is indeed a hexagonal columnar disordered phase (Col<sub>hd</sub>).

It is also interesting to note from table 1, that compound **1** shows only a cubic phase while compound **5** is also monomesomorphic and exhibits a hexagonal columnar phase. The clearing enthalpy for the columnar phase was much less than what was observed for

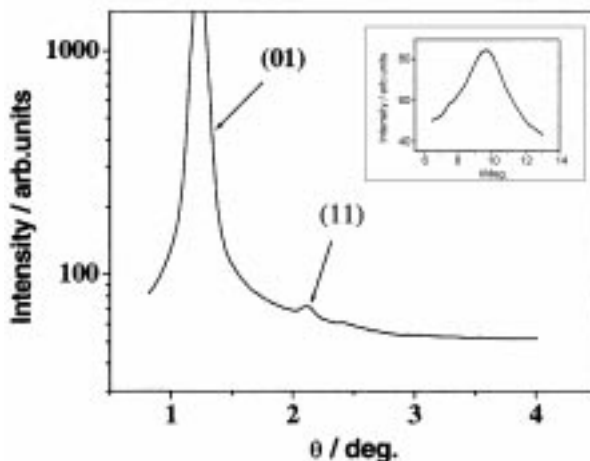
the cubic phase and was about  $1.61 \text{ kJ mol}^{-1}$ . It is also important to realize that the  $-\text{OH}$  group in this system is crucial for the occurrence of the mesophase. For example, in compound **4**, if the OH group is removed, then the resulting compound has a melting point of  $62^\circ\text{C}$  and does not show a mesophase.

Using the tetracatenar compounds **TC I** as ligands, we synthesized the corresponding copper (II) complexes (TC I Cu) and the transition temperatures obtained are summarized in table 2. It can be seen that compound **6** is non-mesomorphic, while the remaining four are monomesomorphic. Although compound **7** is monotropic, the optical textures of all the four are the same and is typical of that obtained for a hexagonal columnar phase. The spherulites obtained are not as birefringent as that obtained for the ligands. It is somewhat surprising that the transition temperatures are not enhanced as normally observed for calamitic metallomesogens [7], particularly the melting points. The mesophase has been identified to be a hexagonal columnar phase (from XRD) and the clearing enthalpy varies from about  $2.17$  to  $3.2 \text{ kJ mol}^{-1}$ . The cubic phase disappears on complexation. We have replaced copper (II) with palladium (II) in compound **10** and this has a melting point of  $86.0^\circ\text{C}$  and does not show any mesophase.

We have carried out the XRD of an unoriented sample of compound **10**. In the small-angle region, two reflections at  $d_1 = 35.8 \text{ \AA}$  and  $d_2 = 20.7 \text{ \AA}$  were obtained which are in the ratio  $1 : 1/\sqrt{3}$ , indicating a hexagonal columnar phase with a lattice parameter  $a = 41.3 \text{ \AA}$ . The wide-range diffuse peak at about  $4.5 \text{ \AA}$  was also seen indicating the fluidity of the chains. The X-ray angular intensity profile obtained for this compound is shown in figure 5.

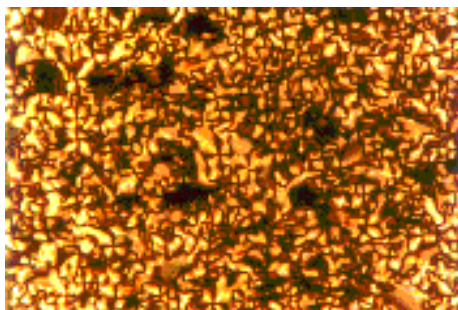
Another important result is that the cubic phase gets eliminated on complexation. It is also not clear as to why the palladium (II) complex does not show any mesophase. Further work is necessary to understand these observations.

From the available evidence of a large number of polycatenar mesogens [6], it is evident that for a  $3(mpm)-1(p)$  system, at least four phenyl rings are necessary for it to exhibit a mesophase. Fully aware of this, we synthesized a tetracatenar compound with only three phenyl rings and as expected this did not show any mesophase and had a m.p. of

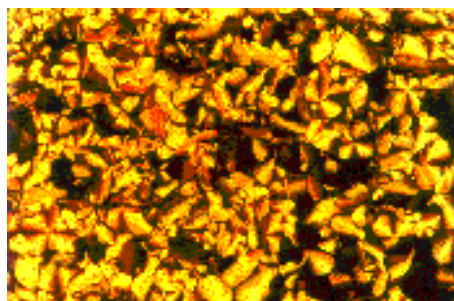


**Figure 5.** X-ray angular intensity profile obtained in the hexagonal columnar phase of copper (II) complex **6**, at  $90^\circ\text{C}$ .

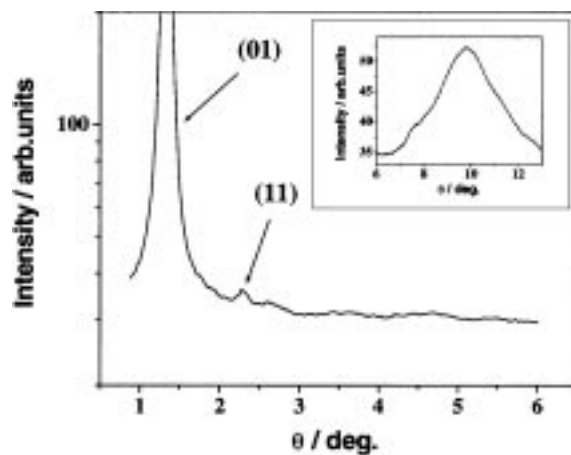
73.5°C. However, very interestingly, both the copper (II) complex **11** and the palladium (II) complex **12** displayed hexagonal columnar disordered phase, though over a narrow range of temperature. The phase identification was carried out using a combination of polarized light optical microscopy, DSC and XRD methods. Surprisingly, the copper (II) complex melted at a lower temperature than the ligand. The clearing enthalpy determined was of the order of 3.36 kJ mol<sup>-1</sup>. It was also found that the mesophases of both the complexes could be supercooled to room temperature. The photomicrographs of the optical textures of the complexes **11** and **12** are shown in figures 6 and 7 respectively. For the palladium (II) complex **12**, which has eight chains, the X-ray diffraction shows a pattern which is typical of a hexagonal columnar structure. In the small-angle region, reflections at  $d_1 = 33.3 \text{ \AA}$  and  $d_2 = 19.3 \text{ \AA}$  could be indexed for a hexagonal columnar phase with a lattice parameter,  $a = 38.5 \text{ \AA}$ . As usual in the wide-angle region a diffuse peak at 4.5 Å was obtained which is due to the melting of the chains. The X-ray angular intensity profile obtained for the mesophase of this complex **12** is shown in figure 8.



**Figure 6.** Optical photomicrograph of the hexagonal columnar phase of copper (II) complex **11**, at 71°C.

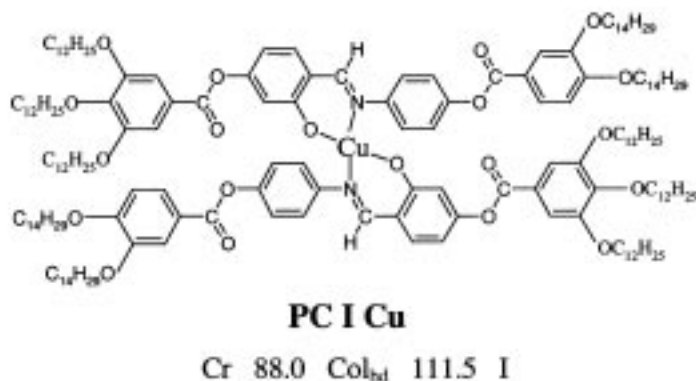
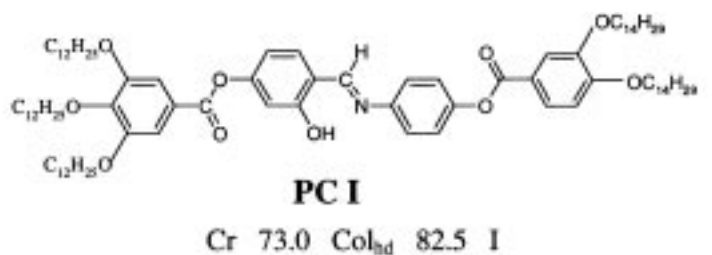


**Figure 7.** Optical photomicrograph of the hexagonal columnar phase of palladium (II) complex **12**, at 77°C.



**Figure 8.** X-ray angular intensity profile obtained in the mesophase of palladium (II) complex **12**, at 77°C.





**Figure 9.** Molecular structure and the transition temperatures (°C) of the pentacatenar ligand **PC I** and its copper (II) complex, **PC I Cu**.

**Table 3.** Transition temperatures (°C) of metal complexes, **TC II M**.

Compound	M	Cr	Col <sub>hd</sub>	I
<b>11</b>	Cu	·	70.0	·
<b>12</b>	Pd	·	75.5	·

### 3.2 Pentacatenar mesogen and its copper complex

We have also investigated the mesomorphic properties of a pentacatenar mesogen, **PC I** [3(*mpm*)-2(*mp*) system] and its copper (II) complex, **PC I Cu**. The molecular structures

and the transition temperatures of these two materials are shown in figure 9. The pentacatenar ligand **PC I** exhibits only one mesophase and this has been identified to be a hexagonal columnar phase, both from textural observations as well as from XRD studies. It has been fairly well-established [6] that for a pentacatenar compound to exhibit a mesophase, at least five phenyl rings are necessary in the core. Perhaps, compound **PC I** represents the first example of a pentacatenar mesogen with only four phenyl rings in the core. **PC I** has a 9.5°C thermal range for the columnar phase. Interestingly, the copper (II) complex of this ligand, **PC I Cu** with ten peripheral alkyl chains also displays a hexagonal columnar phase but over an enhanced thermal range of 23.5°C. Both the melting as well as the clearing temperatures increase on complexation and the mesophase can be supercooled to room temperature. As in the case of the ligand, the mesophase type was determined by the observation of textural patterns and XRD pattern of unoriented samples.

In general, the structure of the columnar phase of both the ligands and the metal complexes are same as the one proposed in the original work [6]. In the present investigations, we find that for the ligands, four molecules are present in each slice or section while two molecules of the complexes are accommodated. It was also found that the lattice parameter  $a$  varies with chain length and the inter-slice distance  $d$  along the column is about 4.5 Å.

#### 4. Conclusions

We have shown that polycatenar compounds can be used as ligands to generate metallomesogens. The metallomesogens obtained from tetracatenars and pentacatenars display a hexagonal columnar phase, and in many cases, these could be supercooled to room temperature. The copper (II) complexes are paramagnetic in nature and their magnetic properties are yet to be investigated. The first pentacatenar mesogen with only four phenyl rings in the core is also reported. The nature of the cubic phase observed in the tetracatenar compounds has not yet been investigated. The complexes containing nickel, platinum and oxovanadium and derived from polycatenars are under preparation and the mesomorphic properties of these will be reported elsewhere.

#### Acknowledgement

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