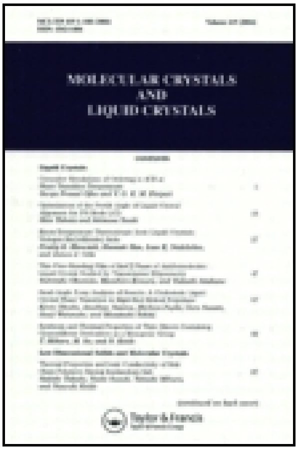

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# Synthesis and Mesomorphic Properties of N(4-n-alkyloxy salicylidene)4′-n-alkylanilines and their Copper Complexes I

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# Synthesis and Mesomorphic Properties of N(4-n-alkyloxy salicylidene)4′-n-alkylanilines and their Copper Complexes I

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A series of metal (Cu) complexes with bidentate Schiff-bases, i.e., N(4-n-alkyloxy salicylidene) 4′-n-alkylanilines obtained by the 1:1 condensation of 4-n-alkyloxy salicylaldehyde and 4-n-alkylanilines, i.e., 4-n-hexylaniline, 4-n-heptylaniline, and 4-n-octylaniline, have been prepared and characterized. The synthesis of the ligands N(4-n-butyloxysalicylidene)-4′-n-alkylanilines as well as the complexes and characterization by thermal microscopy for mesomorphism are presented. The ligands are found to exhibit interesting smectic phases (mostly tilted phases) and polymorphism, while the complexes showed orthogonal smectic A, smectic B, and smectic E phases. The mesomorphic range as well as the polymorphism decreases with increase in chain length. However, the coordination with copper leads to thermally stable metallomesogens possessing larger mesomorphic range but with a reduced number of mesomorphic phases.

Keywords Schiff bases, metallomesogens, liquid crystals, copper complexes, mesomorphism

## INTRODUCTION

Although the great potential of metallomesogens as advanced molecular materials has been recognized, the mesomorphic properties of transition metal complexes have not been fully exploited [1–3]. The characteristic properties of metal atoms as well as the complex but subtle mesomorphic properties of the Schiff base ligands in the reported examples have become quite diverse over the past decade [4–9]. A systematic study of mesomorphic

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properties, i.e., characterization of the ligands, the influence of the complexation of a metal with the ligands to form coordination compounds, thereby affecting the mesomorphic properties of the ligands can establish not only the molecular structure-function relationships but also the molecular design principles toward specific material functions. A variety of substituted N-salicylidene anilines complexes with Cu (II) have been reported [10–18] exhibiting nematic, smectic A, smectic C, smectic C*, smectic B, and smectic E phases.

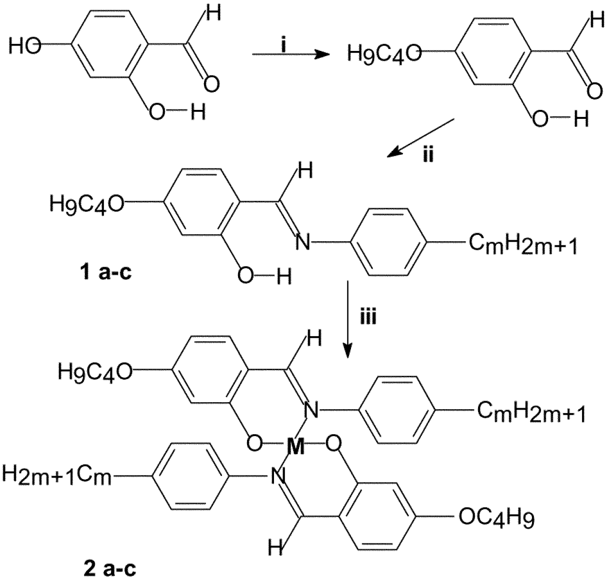
The Schiff bases or imines, i.e., N(4-n-alkyloxybenzylidene) 4′-n-alkylanilines popularly known as *n*O.*m* series, exhibit not only complex but also subtle polymesomorphism [19]. The metallomesogens, derived from *n*O.*m* compounds with Palladium, i.e., dinuclear ortho palladated complexes formed with different bridging groups, exhibit ordered mesophases [20–22]. The introduction of ortho-hydroxyl functional group in benzylidene moiety manifesting the intramolecular H-bonding not only enhances the stability of the imines but also promotes the tilted smectic phases. However, most of the reported complexes are derived from N(4-n-alkyloxy salicylidene)-4′-n-alkylanilines (here after abbreviated as nO(OH).m compounds [10,11], with $n = 12$, $m = 1-4$, 6 and 8; $n = m = 2, 6, 10$ and 14; $n = 2, 6, 14$, $m = 10$; $n = 10$, $m = 2, 4, 6$ and 14 and $n = 7$, $m = 4$) with the metals Cu(II) [10–16], Ni(II), VO(II) [17] and Pd(II) [18]. The studies on Schiff base copper(II) complexes containing alkyl anilines are comparatively meagre, according to earlier reports by Serrano et al. and Ghedini et al.

Enhancement of liquid crystalline behavior that relies on the presence of anisotropic dispersion forces to stabilize the mesophase and hence either shape anisotropy or lateral polar group introduction, which can enhance the molecular polarizability as well as stabilize the molecule, contribute to the above. Our earlier studies on *n*O.*m* compounds, in particular 4O.*m* series, revealed that $m = 4$ to 10 and 12 all exhibited NAB variant except 4O.6 and 4O.7, which exhibited NAC and NACB variants respectively. Introduction of hydroxyl group in ortho position not only enhances the transverse dipole moment but also intramolecular as well as intermolecular interactions, which can contribute to stabilizing the molecule. These ideas motivated us to undertake a more detailed study of Schiff's bases, their characterization, and their complexes with different metals and molecular structure-function relationships. As part of it, the present paper describes the synthesis of lower homologues N(4-n-butyloxy salicylidene) 4′-n-alkylanilines 4O(OH).6, 4O(OH).7, and 4O(OH).8 and their complexes with Copper (II), phase transition temperatures, and characterization of the phases.

## EXPERIMENTAL

Ligands **1a** to **1c** were synthesized in a two step reaction in which the hydroxyl group in the 4-position in 2,4-dihydroxybenzaldehyde is first replaced by an alkoxy chain, which was followed by preparation of Schiff base by the reaction of the aldehyde with an alkyl aniline following the procedures well documented in literature and as presented in Scheme 1.

2,4-dihydroxybenzaldehyde (leq) and 1-bromobutane (leq.) in absolute ethanol with KOH (leq) as the base were refluxed for 3 h to yield 4-n-butyloxy-2-hydroxybenzaldehyde, along with a few side products. The crude 4-n-butyloxy-2-hydroxybenzaldehyde was purified by column chromatography with silica gel (100–200 mesh) and petroleum ether as eluent, and then condensed with 4-n-alkylaniline in absolute ethanol using a few drops of glacial acetic acid as catalyst. The Schiff bases N-(4-n-butyloxy salicylidene)-4′-n-alkylanilines (n-alkyl = n-hexyl, n-heptyl and n-octyl) were purified by crystallizing from absolute ethanol. The overall yield varied between 60 ∼ 70%. The ligands were characterized by NMR, IR spectroscopy. The copper complexes **2a**–**2c** were prepared as follows: To the Schiff base dissolved in absolute ethanol a solution of the copper acetate dihydrate in



SCHEME 1 Reagents and Conditions: i) RBr,Abs EtOH, Δ 3 h ii) Abs EtOH, AcOH, Δ 3 h. iii) $Cu(OAc)_2.2H_2O$, KOH, EtOH.

absolute ethanol and an equivalent amount of KOH were added, and the mixture was stirred at room temperature for 3 h to yield a greenish solid, which was filtered. The complexes are recrystallized from ethanol-chloroform mixture with yields of 80%. The Infrared spectra of the metal complexes show a stretching band around 1609 $\text{cm}^{-1}$ for all the copper complexes, which is assigned to $\nu_{(C=N)}$; it is found that this band appears at 1622 $\text{cm}^{-1}$ for free Schiff bases. All phase behaviors are determined using optical polarizing microscopy with Nikon optiphot-2-pol attachment with a hot stage.

All chemicals were used as received without further purification. Organic reagents were obtained from M/S TCI and E Merck. The liquid crystalline behavior of all the ligands and the complexes was studied by thermal microscopy. The phase transition temperatures of ligands as well as metal complexes are summarized in Table 1.

**1a: 4O(OH).6**

$$\text{Solid} \xrightleftharpoons{<30\,^{0}\text{C}} S_G \xrightleftharpoons{36\,^{0}\text{C}} S_3 \xrightleftharpoons{50\,^{0}\text{C}} S_C \xrightleftharpoons{62\,^{0}\text{C}} S_A \xrightleftharpoons{72.4\,^{0}\text{C}} N \xrightleftharpoons{91\,^{0}\text{C}} I$$

**1b: 4O(OH).7**

$$\text{Solid} \xrightleftharpoons{37\,^{0}\text{C}} S_4 \xrightleftharpoons{40\,^{0}\text{C}} S_3 \xrightleftharpoons{72\,^{0}\text{C}} S_2 \xrightleftharpoons{78\,^{0}\text{C}} N \xrightleftharpoons{84\,^{0}\text{C}} I$$

**1c: 4O(OH).8**

$$\text{Solid} \xrightleftharpoons{50\,^{0}\text{C}} S_3 \xrightleftharpoons{60\,^{0}\text{C}} S_2 \xrightleftharpoons{72\,^{0}\text{C}} S_A \xrightleftharpoons{86\,^{0}\text{C}} N \xrightleftharpoons{98\,^{0}\text{C}} I$$

**2a: (4O(OH).6)$_2$Cu**

$$\text{Solid} \xrightleftharpoons{72\,^{0}\text{C}} S_A \xrightleftharpoons{168\,^{0}\text{C}} I$$

**2b: (4O(OH).7)$_2$Cu**

$$\text{Solid} \xrightleftharpoons{65\,^{0}\text{C}} S_E \xrightleftharpoons{68\,^{0}\text{C}} S_B \xrightleftharpoons{164\,^{0}\text{C}} S_A \xrightleftharpoons{165\,^{0}\text{C}} I$$

**2c: (4O(OH).8)$_2$Cu**

$$\text{Solid} \xrightleftharpoons{40\,^{0}\text{C}} S_E \xrightleftharpoons{56\,^{0}\text{C}} S_B \xrightleftharpoons{148\,^{0}\text{C}} S_A \xrightleftharpoons{165\,^{0}\text{C}} I$$

TABLE 1 Transition temperatures and mesomorphic phases of the ligands and complexes.

## RESULTS AND DISCUSSION

### Ligands Mesomorphism

The phase transition temperatures of the N-(4-n-butyloxysalicylidene)-4′-n-alkylanilines, hereafter abbreviated as $n$O(OH).$m$ compounds, where $n = 4$ and $m = 6, 7$ and 8 are presented in Table 1. The compounds exhibit interesting optical textures.

#### *4O(OH).6*

On cooling the sample from isotropic liquid, marble and threaded textures appeared below 91°C, characterizing a nematic phase, followed by smectic A ($S_1 = S_A$) phase with focal conic fan texture at 72.4°C, and smectic C ($S_2 = S_c$) phase exhibiting schlieren and broken focal conic fan textures below 62°C. Upon further cooling, the schlieren texture becomes dressed by parallel lines following the C field. The microphotograph is shown in Figure 1. These lines have been interpreted [23] as layer undulations caused by stresses due to thermal contraction, and the contraction may be exceptionally large because of large increase in tilt upon cooling in $S_c$ phase. Such sudden increase in tilt angle leading to layer contraction at the onset of $S_c$ phase is observed earlier [23, 24]. On further cooling of smectic C phase, these undulation lines disappear at 50°C leading to $S_3$ phase. The microphotograph of the texture, which is shown in Figure 2, of the $S_3$ phase resembles the texture for smectic M phase [25] reported in 2-chloro-n-alkyl carboxylic acid esters of 2-(4-hydroxyphenyl)-5-(4-alkyloxyphenyl)-pyrimidines. On further cooling a $S_4$ phase appeared at 36°C. The $S_4$ phase exhibits mosaic texture, which is characteristic of $S_J$ phase. Further miscibility studies are in progress to characterize the $S_3$ and $S_4$ phases.

#### *4O(OH).7*

On cooling the sample 4O(OH).7 from isotropic liquid the nematic phase appeared at 84°C, exhibiting marble and threaded textures characteristic of nematic phase. With further cooling there appears a $S_2$ smectic phase at 78°C with a broken chevron-like texture with crosshatched pattern or gridlike pattern. The texture of $S_2$ phase at 75°C is displayed in Figure 3 and resembles the texture reported for a smectic C phase with double undulations [23]. In these compounds there is a possibility of intermolecular H-bonding, which may promote the spiral or helical structure in smectic C phase to exhibit such striped textures on cooling. These striped textures

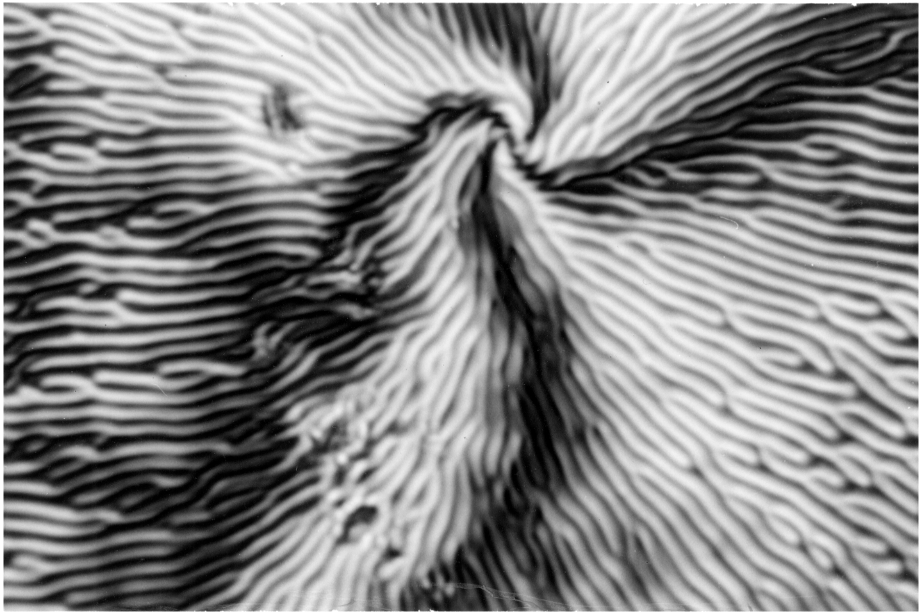


FIGURE 1 Smectic schlieren texture with undulation line 4O(OH).6 at 60°C.

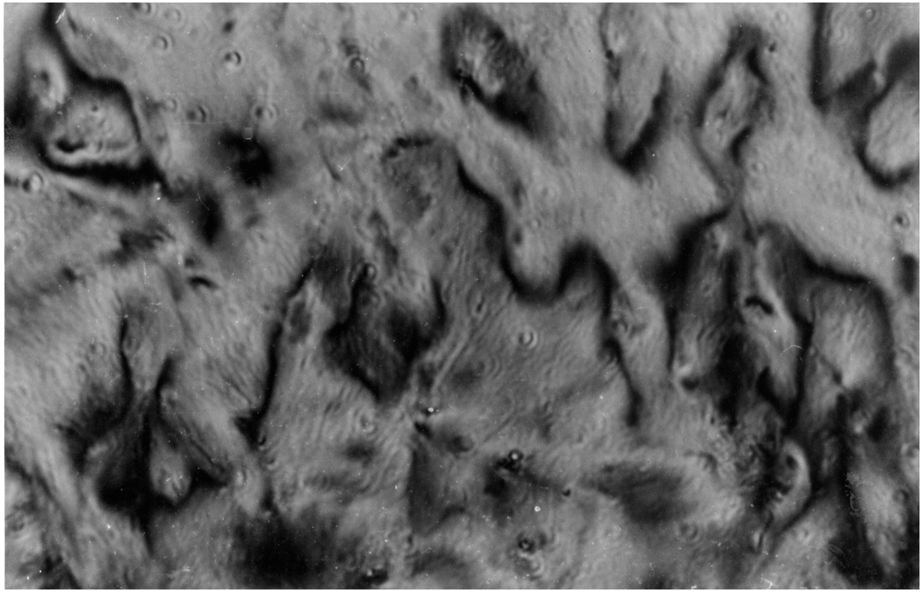


FIGURE 2 Schlieren texture ($S_3$) of smectic phase of 4O(OH).6 at 45°C.

resemble those [26] that are exhibited by the racemic (R*,S*)-$\beta$-MeTFMHPOSC possessing helical structure in smectic C* phase. The contraction of the smectic layers of the tilted phase may be exceptionally large because of sudden manifestation of large tilt upon cooling. On further cooling there appears another smectic phase, $S_3$, at 72°C with a change from broken chevron-like texture to a gridlike pattern with domain walls, which is displayed in Figure 4. Since the smectic M phase is a tilted phase possessing short-range positional order in the smectic layers, and the structural order is similar to $S_I$ and $S_F$ phases with subtle differences, the $S_M$ phase follows a phase sequence of $S_C - S_M$ or $S_C - S_M - S_J$ in compounds possessing helical structures. Although it is conceivable that any of the phase variants $S_CS_FS_G$ or $S_CS_IS_G$ or $S_CS_MS_J$ is possible, there is a reason based on optical textures to believe that it is a $S_CS_MS_J$ phase variant. Hence we assign that this phase may be smectic M. This phase is continued up to 40°C, and there appeared a $S_4$ smectic phase below this temperature resembling the characteristic mosaic texture of smectic J phase. Further studies are in progress to confirm the $S_2, S_3$, and $S_4$ phases by miscibility studies.

### *4O(OH).8*

On cooling the sample 4O(OH).8 from isotropic liquid phase it transformed into the nematic phase at 98°C, showing threaded texture followed by smectic C phase at 86°C exhibiting a characteristic schlieren texture. Further cooling of the sample yielded characteristic texture of smectic M phase at 72°C and smectic J phase at 60°C, and finally crystallizing at 50°C to solid state.

## Influence of OH Group

The effect of replacing the hydrogen by hydroxyl group in the ortho position to imine linkage of the aldehyde moiety not only promotes intramolecular hydrogen bonding but also stabilizes thermally. The resultant transverse dipole moment promotes the tilted smectic phases as well as large smectic C phase ranges in comparison to its unsubstituted analogues (smectic C range is $1 \sim 2$°C in 4O.6 and 4O.7 of *n*O.*m* compounds). The increased number, as well as thermal ranges of tilted phases, indicates weak intermolecular forces of Vander Walls type. Further work is in progress to infer the nature of intermolecular forces responsible for the formation of tilted phases in *n*O(OH).*m* compounds.

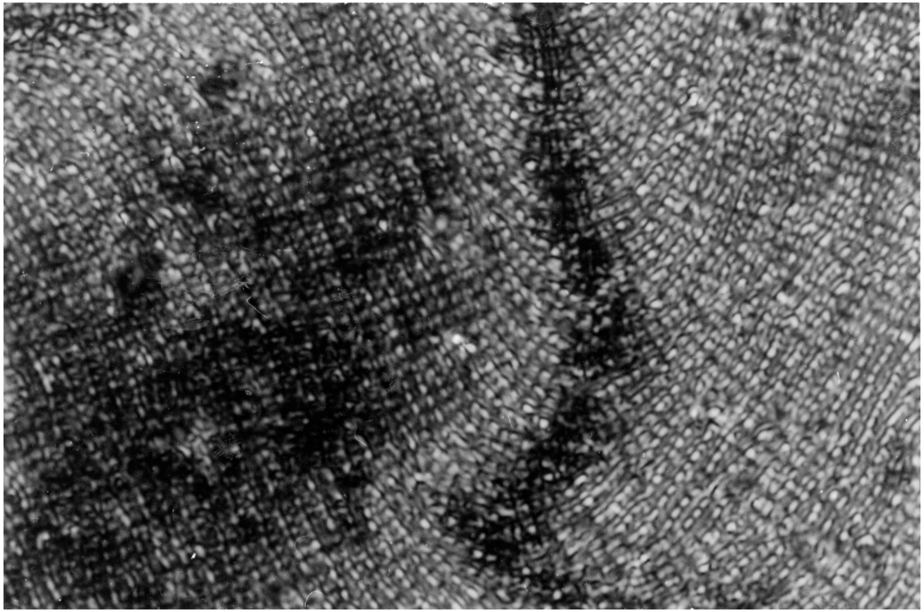


FIGURE 3 Smectic C schlieren texture with crosshatched pattern manifested from double undulation line 4O(OH).6 at 75°C.

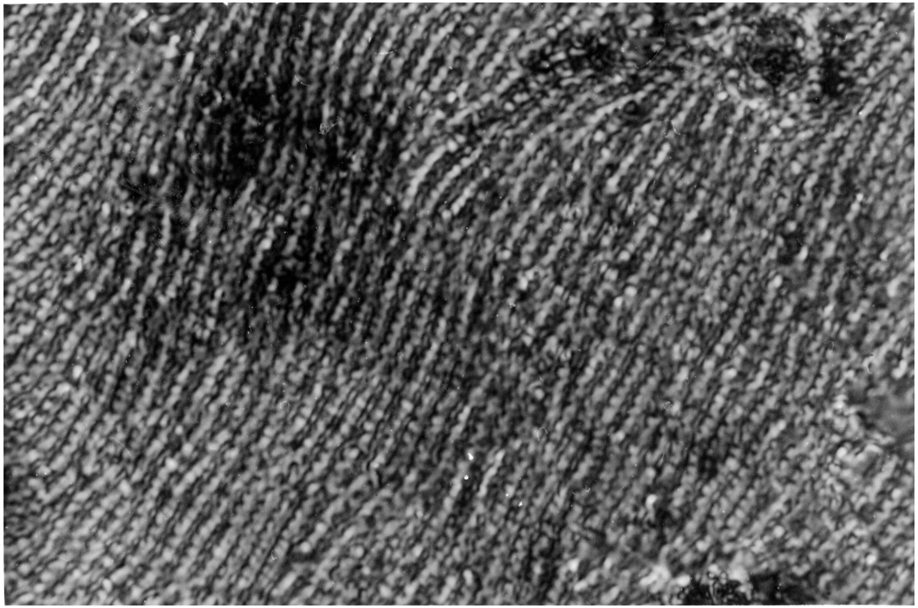


FIGURE 4 Smectic ($S_3$) schlieren texture exhibiting gridlike pattern with domain walls manifested from undulation line 4O(OH).6 at 70°C.

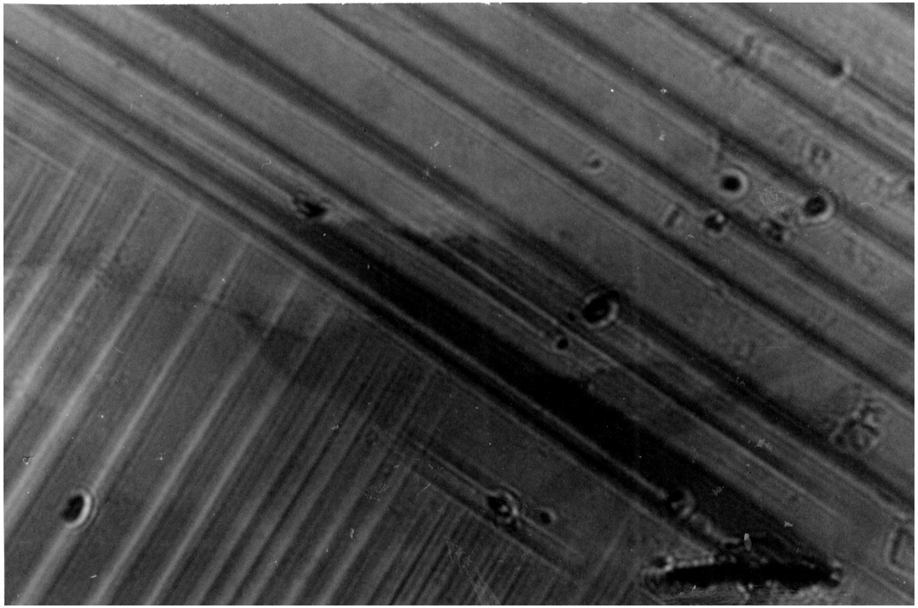


FIGURE 5 Smectic E domain like texture of $Cu[4O(OH).8]_2$ at 60°C.

## COMPLEXES

As it can be seen form the data presented in Table 1, the copper compounds of different ligands possess similar liquid crystalline properties:

1. The lower homologue exhibits smectic A phase only, while the other two complexes exhibit ABE variant exhibiting fan, smooth fan, and domain-like textures, respectively. The texture of smectic E is shown in Figure 6.
2. Almost same clearing temperatures with an increase in mesomorphic-isotropic transition temperatures by about 75 ± 6°C in comparison with the ligands. This increase in clearing temperature is higher than the increase in clearing temperature of 12O(OH).*m* series [11]. Moreover, none of the complexes exhibit the tilted phases that are exhibited by the ligands.
3. The mesomorphic range and the mesomorphic phases decrease with the increase in chain length. However, the coordination leads to larger mesomorphic range as well as the number of mesomorphic phases.

## CONCLUSIONS

The number of liquid crystalline phases exhibited by the ligands is totally suppressed by the coordination. Secondly, the complexes exhibited only orthogonal smectic phases. Thirdly, the clearing temperatures increase by $70 \sim 80°C$ on coordination, inferring thermal stability on coordination.

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