

Contents lists available at ScienceDirect

Journal of Molecular Structure



journal homepage: www.elsevier.com/locate/molstruc

Synthesis, 2D NMR and X-ray diffraction studies on Cu(II) and Ni(II) complexes with ligands derived from azobenzene-cored Schiff base: Mesomorphic behaviors of Cu(II)–phenolates and crystal structure of bis[4-(4-alkoxy-2-hydroxybenzylideneamino)azobenzene]copper(II)

Guan-Yeow Yeap^{a,*}, Boon-Teck Heng^a, Masaki Kakeya^b, Daisuke Takeuchi^b, Ewa Gorecka^c, Masato M. Ito^d

^a Liquid Crystal Research Laboratory, School of Chemical Sciences, Universiti Sains Malaysia, 11800 Minden, Penang, Malaysia

^b Chemical Resources Laboratory (Mailbox R1-03), Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan

^c Department of Chemistry, Warsaw University, Al.Zwirki I Wigury 101, 02-089 Warsaw, Poland

^d Department of Environmental Engineering for Symbiosis, Faculty of Engineering, Soka University, Hachioji, Tokyo 192-8577, Japan

ARTICLE INFO

Article history: Received 9 January 2011 Received in revised form 19 May 2011 Accepted 19 May 2011 Available online 13 June 2011

Keywords: Cu(II)-phenolate complexes Ni(II) complexes FTIR NMR X-ray diffraction Mesomorphic behavior

1. Introduction

ABSTRACT

Two new homologous series of copper(II) and nickel(II) complexes derived from bidentate Schiff bases 4-(4-alkoxy-2-hydroxybenzylideneamino)azobenzene have successfully been synthesized. Their molecular structures were elucidated by FT-IR, ¹H and ¹³C NMR along with ¹H–¹H COSY, ¹H–¹³C HMQC, ¹H and ¹³C HMBC. Mesomorphic behaviors of ligands and metal complexes have been investigated by differential scanning calorimetry and polarizing optical microscope. All ligands and their copper complexes exhibit exclusively the mesomorphic properties. The X-ray diffraction studies have confirmed the presence of smectic A (SmA) phase in copper(II)–phenolate complexes. The molecular structure of bis[4-(4-alkoxy-2-hydroxybenzylideneamino)azobenzene]copper(II) have been determined by using X-ray crystallographic techniques. It was found that the ligands have square planar configuration around the Cu center ion as evident by the N–Cu–N and O–Cu–O angles of 180°.

© 2011 Elsevier B.V. All rights reserved.

Liquid crystal have been known for many decades but the new or modified process for the obtainment of new chemical compounds capable of exhibiting mesomorphic properties has only been accelerated in the last 20 years. The innovative effort in searching for these compounds has inspired the researchers to diversify into metal containing liquid crystals or metallomesogens which possess various ranges of metal-base coordination modes [1]. The importance from the synthesis of metallomesogens can generally be associated with the advantage of combining the properties of liquid crystal system with those of transition metal. The presence of metal ions can induce the changing of non-mesogenic compounds to compounds with mesogenic properties [2]. In general, the metallomesogens have new geometrical shapes as the metal ions are able to adopt various geometries ranging from square planar, folder square, lantern, pyramidal and octahedral geometrical shapes [3,4]. Furthermore, the presence of metal ions can lead to richness in terms of oxidation state, color and magnetism [5].

In 1997, Tantrawong and co-worker had successfully synthesized metal containing liquid crystal with the potential application in optical storage [6]. Liu and co-worker have found that metallomesogens have widespread use as stationary phase in gas chromatographic application due to the benefits of coupling the usual analytical strengths of gas chromatography with the unique structure and shape selectivity properties of the liquid crystalline phase [7]. Recently, Huang and co-worker synthesized a metallomesogen of a polycatenar oxazoline copper(II) complex that could exhibit a columnar mesophase and employed as the stationary phase for the GC separation with polycyclic aromatic hydrocarbons as model compound [8].

Besides, the azo-based polymeric liquid crystals and its metalcontaining derivatives have also been studied extensively in recent years because these materials are capable of changing the molecular shape through the reversible *cis-trans* isomerization under the influence of UV or photoirradiation. The thermo- and photoisomerization of azobenzene derivatives are important for the development of information recording system such as

^{*} Corresponding author. Fax: +60 4 6574854.

E-mail addresses: gyyeap@usm.my, gyyeap_liqcryst_usm@yahoo.com (G.-Y. Yeap).

^{0022-2860/\$ -} see front matter \circledcirc 2011 Elsevier B.V. All rights reserved. doi:10.1016/j.molstruc.2011.05.036

high-density optical data storage, optical switching, display and nonlinear optics [9,10]. However, it has been claimed that the molecules with -N=N- group in mesophase prefer the *trans* conformation as that/those reported for photoexcited azo-dye induced torque in N liquid crystals [11]. Another interesting

feature of azobenzene compound lies on its potential to form rod-like molecules leading to the materials exhibiting liquid crystalline properties [11].

The Schiff bases derived from substituted salicylaldehyde can serve as ligands which form N–O chelates and have been widely



Scheme 1. Synthetic pathway towards the formation of Cu(II) and Ni(II) complexes.

Table 1			
¹ H NMR chemical	shift (ppm)	of ligands	1a-1j.

Atom	Atom Chemical shift (ppm)									
	1a	1b	1c	1d	1e	1f	1g	1h	1i	1j
H1 and H2	6.52-6.55 (m)	6.51-6.55 (m)	6.51-6.55 (m)	6.52-6.54 (m)	6.52-6.54 (m)	6.51-6.54 (m)	6.51-6.55 (m)	6.51-6.55 (m)	6.52-6.54 (m)	6.51-6.55 (m)
H3	7.32-7.34 (d)	7.31-7.33 (d)	7.30-7.33 (d)	7.28-7.33 (d)	7.28-7.33 (d)	7.31-7.33 (d)	7.31-7.33 (d)	7.30-7.33 (d)	7.28-7.33 (d)	7.30-7.33 (d)
H4 and H5	7.41-7.43 (d)	7.40-7.43 (d)	7.40-7.43 (d)	7.40-7.43 (d)	7.40-7.43 (d)	7.41-7.43 (d)	7.41-7.43 (d)	7.40-7.43 (d)	7.40-7.43 (d)	7.40-7.43 (d)
H10, H11 and H12	7.46-7.57 (m)	7.45-7.57 (m)	7.46-7.57 (m)	7.45-7.57 (m)	7.45-7.57 (m)	7.46-7.57 (m)	7.46-7.57 (m)	7.46-7.57 (m)	7.45-7.57 (m)	7.45-7.56 (m)
H8 and H9	7.94-7.96 (dd)	7.93-7.96 (dd)	7.93-7.96 (dd)	7.93-7.96 (dd)	7.93-7.96 (dd)	7.93-7.96 (dd)	7.93-7.96 (dd)	7.93-7.96 (dd)	7.94-7.96 (dd)	7.94-7.96 (dd)
H6 and H7	8.00-8.03 (d)	8.00-8.03 (d)	8.01-8.03 (d)	8.01-8.03 (d)	8.01-8.03 (d)	8.00-8.03 (d)	8.01-8.03 (d)	8.01-8.03 (d)	8.01-8.03 (d)	8.01-8.03 (d)
H13	8.63 (s)	8.63 (s)	8.63 (s)	8.62 (s)	8.62 (s)	8.62 (s)	8.62 (s)	8.63 (s)	8.63 (s)	8.63 (s)
H14	13.62 (s)	13.60 (s)	13.60 (s)	13.63 (s)	13.63 (s)	13.61 (s)	13.60 (s)	13.61 (s)	13.63 (s)	13.63 (s)
H1′	4.02-4.05 (t)	4.02-4.05 (t)	4.02-4.05 (t)	4.02-4.05 (t)	4.02-4.05 (t)	4.02-4.05 (t)	4.02-4.05 (t)	4.02-4.05 (t)	4.02-4.05 (t)	4.02-4.05 (t)
H2'—Hn"	1.31-1.87 (m)	1.29-1.87 (m)	1.25-1.88 (m)	1.25-1.85 (m)	1.25-1.85 (m)	1.25-1.87 (m)	1.29-1.87 (m)	1.25-1.88 (m)	1.25-1.86 (m)	1.25-1.85 (m)
H (methyl)	0.88-0.91 (t)	0.88-0.91 (t)	0.88-0.92 (t)	0.89–0.93 (t)	0.89–0.93 (t)	0.88-0.91 (t)	0.88-0.92 (t)	0.88-0.92 (t)	0.89–0.93 (t)	0.89–0.93 (t)

TMS as internal standard.

s, singlet; d, doublet; dd, doublet of doublet; m, multiplets.

Table	2
-------	---

¹³C NMR chemical shift (ppm) of compound ligand **1a–1j**.

Atom	Chemical shift (ppm)									
	1a	1b	1c	1d	1e	1f	1g	1h	1i	1j
C1	108.33	108.35	108.35	108.34	108.35	108.35	108.35	108.35	108.34	108.35
C2	102.10	101.97	101.98	101.98	101.97	101.98	101.97	101.97	101.98	101.97
C3	134.19	134.17	134.18	134.19	134.20	134.17	134.17	134.18	134.18	134.19
C4 and C5	122.14	122.12	122.13	122.13	122.12	122.14	122.14	122.13	122.12	122.12
C6 and C7	124.64	124.63	124.63	124.62	124.62	124.64	124.64	124.62	124.63	124.62
C8 and C9	123.24	123.22	123.23	123.24	123.24	123.23	123.22	123.23	123.23	123.24
C10 and C11	129.51	129.50	129.49	129.49	129.48	129.51	129.50	129.51	129.49	129.50
C12	131.23	131.32	131.33	131.34	131.34	131.33	131.32	131.33	131.34	131.34
C13	162.39	162.40	162.40	162.38	162.40	162.40	162.40	162.38	162.38	162.40
C14	164.48	164.49	164.50	164.51	164.56	164.48	164.49	164.49	164.51	164.51
C15	164.44	164.45	164.44	164.43	164.46	164.44	164.44	164.45	164.43	164.46
C16	113.13	113.14	113.14	113.13	113.15	113.13	113.14	113.15	113.13	113.14
C17	153.15	153.14	153.14	153.13	153.14	153.14	153.14	153.13	153.13	153.14
C18	151.16	151.16	151.17	151.18	151.17	151.16	151.16	151.16	151.18	151.18
C19	151.31	151.30	151.29	151.30	151.30	151.31	151.30	151.30	151.30	151.29
C1′	68.72	68.74	68.74	68.75	68.75	68.73	68.74	68.74	68.74	68.75
C2'-Cn'	32.24-23.08	32.31-23.06	32.32-23.09	32.30-23.09	32.32-23.10	32.20-23.02	32.21-23.02	32.21-23.04	32.30-23.05	32.32-23.08
C (methyl)	14.49	14.51	14.50	14.50	14.49	14.49	14.49	14.50	14.50	14.49

used in the synthesis of metallomesogen. In view of the diversity of substituents thus introduced, a great variety of mesogenic complexes has been reported [12]. In this paper we report the preparation of new copper(II) and nickel(II) complexes derived from new bidentate Schiff bases. The structure for all the title compounds were characterized by FT-IR and NMR (¹H, ¹³C, COSY, HMQC and HMBC). The phase transition temperature and enthalpy values of the title compounds were measured by differential scanning calorimetry (DSC) and the textures of the mesophases were studied using polarizing optical microscope (POM). The study of the molecular anisotropy in relation to the smectogenic behavior and intermolecular interaction has been carried out by X-ray diffraction analysis.

2. Experimental

1-Bromooctane, 1-bromodecane, 1-bromododecane, 1-bromotetradecane and 1-bromohexadecane were purchased from Merck. 4-Aminoazobenzene was purchased from Aldrich-Chemical while copper(II) acetate monohydrate and 2,4-dihydroxybenzaldehyde were obtained from Acros Organic. Potassium carbonate was purchased from Systerm.

Whilst the synthesis of 4-(2,4-dihydroxybenzylideneamino)azobenzene was carried out using the method as reported by Ispir [13], the preparation of ligands 4-(4-alkoxy-2-hydroxybenzylideneamino)azobenzene, **1a–1j** and their corresponding Cu(II) and Ni(II) will be described for the first time in this report.

2.1. Synthesis

2.1.1. Synthesis of 4-(4-alkoxy-2-

hydroxybenzylideneamino)azobenzene, 1a-1j

To a mixture containing 0.50 g (1.0 mmol) of 4-(2,4-dihydroxybenzylideneamino)azobenzene in acetone, two equivalent of potassium carbonate and 2.2 M of appropriate 1-bromoalkane were added. The reaction mixture was heated for overnight at 60 °C under continuous stirring. The resulting mixture was left for evaporation at room temperature. The potassium carbonate was then dissolved in water and separated from the crude precipitate via filtration. The precipitate was then dried and recrystallized from *n*-hexane.

The yield and elemental analytical data for ligands **1a–1j** are summarized as follows:

1a: Yield 46%. Elemental analysis/%: Found C 75.92, H 7.32, N 9.80; calculated (C₂₇H₃₁N₃O₂) C 75.52, H 7.23, N 9.79.

1b: Yield 52%. Elemental analysis/%: Found C 76.45, H 7.68, N 9.21; calculated (C₂₉H₃₅N₃O₂) C 76.15, H 7.66, N 9.19.

1c: Yield 50%. Elemental analysis/%: Found C 77.01, H 8.14, N 8.70; calculated (C₃₁H₃₉N₃O₂), C 76.70, H 8.04, N 8.66.

1d: Yield 53%. Elemental analysis/%: Found C 77.59, H 8.58, N 8.19; calculated (C₃₃H₄₃N₃O₂), C 77.19, H 8.38, N 8.18.

1e: Yield 50%. Elemental analysis/%: Found C 77.96, H 8.73, N 7.81; calculated (C₃₅H₄₇N₃O₂), 1473 (N=N), C 77.63, H 8.69, N 7.76.

1f: Yield 53%. Elemental analysis/%: Found C 74.20, H 6.54, N 10.69; calculated (C₂₄H₂₅N₃O₂) C 74.43, H 6.46, N 10.85.

1g: Yield 52%. Elemental analysis/%: Found C 74.69, H 6.77, N 10.57; calculated (C₂₅H₂₇N₃O₂) C 74.82, H 6.72, N 10.47.

1h: Yield 60%. Elemental analysis/%: Found C 75.24, H 7.06, N 9.81; calculated (C₂₆H₂₉N₃O₂), C 75.19, H 6.98, N 10.12.

1i: Yield 58%. Elemental analysis/%: Found C 75.73, H 7.51, N 9.21; calculated (C₂₈H₃₃N₃O₂) C 75.86, H 7.44, N 9.48.

1j: Yield 50%. Elemental analysis/%: Found C 76.35, H 7.93, N

8.77; calculated (C₃₀H₃₇N₃O₂), C 76.44, H 7.85, N 8.91.

2.1.2. Synthesis of copper(II) complexes, 2a-2e

An ethanolic solution (10 ml) of copper(II) acetate (1.0 mmol) was added dropwise to a hot ethanolic solution (50 ml) of compound **1** (1.0 mmol) in round bottom flask. The mixture was refluxed for 6 h at 70 °C and then cooled to room temperature. The brown precipitate was collected by filtration and recrystallized from chloroform–ethanol (1:1).

The yield and elemental analytical data for complexes **2a–2j** are summarized as follow:

2a: Yield 80%. Elemental analysis/%: Found C 70.67, H 6.65, N 9.26; calculated (C54H60N6O4Cu), C 70.46, H 6.53, N 9.14. 2b: Yield 75%. Elemental analysis/%: Found C 71.66, H 7.03, N 8.73; calculated (C₅₈H₆₈N₆O₄Cu), C 71.35, H 6.97, N 8.61. 2c: Yield 70%. Elemental analysis/%: Found C 72.42, H 7.57, N 8.16; calculated (C₆₂H₇₆N₆O₄Cu), C 72.13, H 7.37, N 8.14. 2d: Yield 80%. Elemental analysis/%: Found C 73.21. H 7.87. N 7.88; calculated (C₆₆H₈₄N₆O₄Cu), C 72.82, H 7.72, N 7.72. 2e: Yield 80%. Elemental analysis/%: Found C 73.87, H 8.17, N 7.46; calculated (C₇₀H₉₂N₆O₄Cu), C 73.46, H 8.05, N 7.35. 2f: Yield 82%. Elemental analysis/%: Found C 69.06, H 5.76, N 10.06; calculated (C₄₈H₄₈N₆O₄Cu), C 68.95, H 5.74, N 10.05. 2g: Yield 79%. Elemental analysis/%: Found C 69.37, H 5.98, N 9.72; calculated (C₅₀H₅₂N₆O₄Cu), C 69.49, H 6.01, N 9.73. 2h: Yield 81%. Elemental analysis/%: Found C 69.70, H 6.29, N 9.40; calculated (C₅₂H₅₆N₆O₄Cu), C 70.00, H 6.27, N 9.42. 2i: Yield 80%. Elemental analysis/%: Found C 71.24, H 6.98, N 8.79; calculated (C₅₆H₆₄N₆O₄Cu), C 70.93, H 6.75, N 8.87. 2j: Yield 81%. Elemental analysis/%: Found C 71.43, H 7.08, N 8.35; calculated (C₆₀H₇₂N₆O₄Cu), C 71.76, H 7.17, N 8.37.

2.1.3. Synthesis of nickel(II) complexes, 3a-3e

An ethanolic solution (10 ml) of nickel(II) acetate (1.0 mmol) was added dropwise to a hot ethanolic solution (50 ml) of ligands 1a-1e (1.0 mmol) in respective round bottom flask. The mixture was refluxed for 6 h at 70 °C and then cooled to room temperature. The brown precipitate was collected by filtration and recrystallized from chloroform–ethanol (1:1).

The yield and elemental analytical data for complexes **3a–3e** are summarized as follow:

3a: Yield 85%. Elemental analysis/%: Found C 71.10, H 6.57, N 9.20; calculated ($C_{54}H_{60}N_6O_4Ni$), C 70.84, H 6.56, N 9.18. **3b**: Yield 82%. Elemental analysis/%: Found C 71.92, H 7.02, N 8.72; calculated ($C_{58}H_{68}N_6O_4Ni$), C 71.70, H 7.00, N 8.65. **3c**: Yield 76%. Elemental analysis/%: Found C 72.86, H 7.57, N 8.16; calculated ($C_{62}H_{76}N_6O_4Ni$), C 72.47, H 7.40, N 8.18. **3d**: Yield 86%. Elemantal analysis/%: Found C 73.40, H 7.79, N 7.77; calculated ($C_{66}H_{84}N_6O_4Ni$), C 73.15, H 7.58, N 7.76. **3e**: Yield 84%. Elemental analysis/%: Found C 74.10, H 8.09, N 7.39; calculated ($C_{70}H_{92}N_6O_4Ni$), C 73.77, H 8.08, N 7.38.

The synthetic route to prepare all the intermediate and title compounds **1a–1j**, **2a–2j** and **3a–3e** are shown in Scheme 1.

2.2. FTIR measurement

The FTIR data were recorded using a Perkin Elmer 2000-FTIR spectrophotometer in the frequency range $4000-400 \text{ cm}^{-1}$ with sample prepared in KBr disks.

2.3. NMR measurement

The ¹H and ¹³C NMR spectra for ligands **1a–1j** were obtained and substantiated with the aids of two-dimensional ¹H–1H correlation spectroscopy (COSY), ¹H–13C heteronuclear multiple

Table 3	
¹ H– ¹ H correlation from 2D COSY for ligands 1a–1j .	

Ligands	Atom H	COSY
1a-1j	H1 H3 H4 and H5	H3 H1 H6 or H7
	H6 and H7 H8 and H9 H10 and H11 H12	H4 or H5 H10 or H11 H8 or H9 and H12 H10 or H11

quantum correlation (HMQC) and ¹H–13C heteronuclear multiple bond correlation (HMBC). All data were recorded using Brucker Avance 300 and 400 MHz ultrashield spectrometers equipped with ultrashield magnets. Deuterated chloroform (CDCl₃) and dimethysulphoxide (DMSO-d₆) were used as solvent and TMS as internal standard.

2.4. Phase transition temperature and enthalpy values

The phase transition temperature and enthalpy values were measured by Seiko DSC6200R differential scanning calometry at heating and cooling rate of $5 \,^{\circ}\text{C} \,^{\text{min}^{-1}}$ and $-5 \,^{\circ}\text{C} \,^{\text{min}^{-1}}$, respectively.

2.5. Texture observation

The texture was observed using a Carl Zeiss Axioskop 40 polarizing microscope equipped with a Linkam LTS 350 hot stage and

Table 4	
an 111 13 a 111 (a a	1

D	'H- ¹³ C HMQC	and HMBC	correlation	for compou	nd ligands	1a-1j	j.
---	--------------------------	----------	-------------	------------	------------	-------	----

Ligands	Atom	HMQC	НМВС	
		¹ J	² J	зJ
1a–1j	H1 and H2 H3 H4 and H5 H8 and H9 H6 and H7 H13	C1 and C2 C3 C4 or H5 C8 or C9 C6 and C7 C13	C3, C14 and C15 C16 and C1 C6, C17 or C7 C10, C19 or C11 C18, C4 or C5 C16	C16 C12 C3, C14

TMS94 temperature controller. The samples were prepared in thin film sandwiched between glass slide and cover.

2.6. X-ray data collection

The X-ray diffraction patterns were performed with a Bruker D8 Discover and GADDS systems. The homeotropic alignment of the samples were obtained by slow cooling of a drop of the isotropic liquid below the clearing temperature. The X-ray beam was directed almost parallel to the substrate surface and the temperature of the sample was controlled by an accuracy of 0.1°. Finally, the data obtained were analyzed by using Topas software.

2.7. X-ray data collection, structure solution and refinement for Cu(II) complex **2f**

The X-ray crystal structure analytical data were collected using a Rigaku Saturn 70 diffractometer, which uses graphite



Fig. 1. ¹H-¹H connectivities in the COSY spectra for ligand 1e.



Fig. 2. One bond C-H correlation in the HMQC spectra of ligand 1e.

monochromated Mo Ka radiation. The data were collected at a temperature of -159 ± 1 °C to a maximum 2 θ value of 55.0°. A total of 720 oscillation images were collected. A sweep of data was done using ω oscillations from -110.0° to 70.0° in 0.5° steps. The exposure rate was 128.0 ($s/^{\circ}$). The detector swing angle was -20.05° . A second sweep was performed using ω oscillations from -110.0° to 70.0° in 0.5° steps. The exposure rate was 128.0 (s/°). The detector swing angle was -20.05° . The crystalto-detector distance was 45.32 mm. Readout was performed in the 0.137 mm pixel mode. Out of the 15,291 reflections that were collected, 4708 were unique ($R_{int} = 0.0411$). Data were collected and processed using CrystalClear (Rigaku)¹. The linear absorption coefficient, μ , for Mo K α radiation was 5.778 cm⁻¹. An empirical absorption correction was applied which result in transmission factors ranging from 0.462 to 0.966. The data were corrected for Lorentz and polarization effects.

The structure was solved by direct methods [14] and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement on F^2 was based on 4708 observed reflections, 269 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of

$$wR_2 = \left[\sum (w(F_o^2 - F_c^2)^2) / \sum w(F_o^2)^2\right]^{1/2} = 0.1801$$

The standard deviation of an observation of unit weight was 1.11. Unit weights were used. The maximum and minimum peaks on the final difference Fourier map corresponded to 1.23 and $-1.02 \text{ e}^-/\text{Å}^3$, respectively. Neutral atom scattering factors were taken from Cromer and Waber [15]. Anomalous dispersion effects were included in Fcalc [16]; the values for Δf and $\Delta f'$ were those of Creagh and McAuley [17]. The values for the mass attenuation coefficients were those of Creagh and Hubbell [18]. All calculations were performed using the crystal structure crystallographic software package except for the refinement, which was performed using SHELXL97 [19].

3. Results and discussion

3.1. Physical characterization

3.1.1. ¹H and ¹³C NMR spectra assignment for ligands **1a–1j**

Assignment of the ligands **1a–1j** can be based on representative ligand **1e** owing to all of these compounds show similar characteristics as inferred from NMR spectra. The ¹H NMR data from Table 1 shows that the chemical shifts of the aromatic protons are observed at δ = 6.53–8.03 ppm. Proton H1 and H2 appear as

$$R_1 = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.0621$$



Fig. 3. Long range C-H correlation in the HMBC spectra for ligand 1e.

multipletes at δ = 6.52–6.54 ppm whilst the proton pairs in aromatic rings H4 and H5, H6 and H7, H8 and H9, H10 and H11 are equivalent. The doublet at δ = 7.28–7.33 ppm can be ascribed to proton H3 and the appearance of multiplets at δ = 7.45– 7.57 ppm can be ascribed to protons H10, H11, and H12. A singlet observed at δ = 8.62 ppm is corresponded to the azomethine proton H13. The two triplets at $\delta = 0.89 - 0.93$ ppm and $\delta = 4.02 - 0.93$ 4.05 ppm can be ascribed to the methyl proton H16' and proton H1', respectively. The group of protons H2' to H15' are confirmed by the appearance of multiplets at δ = 1.25–1.85 ppm. The hydroxyl protons H14 gives rise to the resonance at δ = 13.60– 13.63 ppm. This observation is in accordance with the analytical results obtained by Ostrovskii et al. [20] whom had reported that the down-field shifts of the hydroxyl proton to $\delta = 13-14$ ppm confirmed the presence of intramolecular hydrogen bonding [21]. The presence of singlet within this range of chemical shift supports the Williamson reaction wherein various alkyl groups from bromoalkanes replaced the H atom from hydroxyl group at para position.

All ligands **1a–1j** show a similar pattern of ¹³C NMR spectra (Table 2). Hence, the discussion based on representative compound **1c** will be reported herein. The signal observed at δ = 151.17 and 151.29 ppm can be attributed to the C18 and C19 which are the carbons attached to N atom in the azobenzene. The signal appears at lower field (δ = 164.50 and 164.45 ppm) can be assigned to C15 and C14 while the signal at δ = 162.40 and 153.14 ppm can be attributed to C13 and C17, respectively. The resonance due to aromatic carbon C4 or C5, C6 or C7, C8 or C9 and C10 or C11 can be located at δ = 122.13, 124.63, 123.23 and 129.49 ppm, respectively. The resonances recorded at δ = 131.33, 134.18, 108.35, 101.98 and 123.34 ppm can be assigned to C12, C3, C1, C2 and C16, respectively. The signal observed in high field at δ = 68.74 and 14.50 ppm can be assigned to C1' and C12' of the methyl group in the alky chain while signal at δ = 23.08–32.31 ppm can be attributed to the carbon from C2' to C11'.

The ¹H–1H COSY NMR has further substantiated the correlation between the equivalent proton pairs with the adjacent protons wherein the cross peak resulting from the correlations appear at the same region (Table 3). Fig. 1 for ligand **1e** exhibits the correlation between H1 with the respective proton H3. The proton H4 or H5 is correlated with proton H6 or H7 and a similar phenomenon can also be found on H8 or H9 which has correlation with H10 or H11. The COSY spectra also reveal that the H1' which is adjacent to O atom in ether group is correlated with H2' and the methyl proton H16' is correlated with H15'. A similar correlation can also be observed for ligands **1a–1j**.

Table 5								
Phase transition	temperature	(°C)	and	associated	enthalpies	$(kJ mol^{-1})$	of	ligand
1a-1i.								

Ligand		K ₁		K_2		SmA		Ν		I	
1a	Heating	•	74.2	•	109.7	•	164.3 ^a	•	176.5 ^a	•	
			(5.4)		(30.5)						
1b	Heating	•	99.6	•	107.1	•	166.9 ^a	•	168.5	•	
			(7.7)		(27.7)				(3.3)		
1c	Heating	•			106.8	•			165.1	•	
					(36.3)				(3.2)		
1d	Heating	•			110.3	•			167.9	•	
					(64.2)				(6.5)		
1e	Heating	•			112.5	•			164.5	•	
					(64.3)				(5.8)		
1f	Heating	•	83.05	•	112.8	•	165.9	•	181.0	•	
			(3.3)		(28.8)		(1.8)		(0.6)		
1g	Heating	•			113.9	•	157.1	٠	193.2ª		
					(23.3)		(1.1)				
1h	Heating	•	75.8	•	110.6	•	151.9 ^a	•	164.8 ^a	•	
			(5.8)		(24.5)						
1i	Heating	•			107.4	•	166.9	•	174.2	•	
					(42.8)		(1.9)		(0.5)		
1j	Heating	•			106.7	•	165.1	•	166.4 ^a	•	
					(33.9)		(1.9)				

K, crystal; N, nematic; Sm A, smectic A; I; isotropic.

^a Denotes transition temperature derived from unresolved peaks.

The ¹H–13C HMQC spectra of compounds **1a–1j** provide information on the interaction between the protons and the carbon atoms which are directly attached to each other (Table 4). As a representative, the discussion will be based on the spectrum for ligand **1e** (Fig. 2). It can be deduced from Fig. 2 that the H1 or H2, H4 or H5, H8 or H9, H6 or H7 in aromatic ring are correlated with C1 or C2, C4 or C5, C8 or C9 and C6 or C7, respectively. Moreover, the one-bond ¹³C–1H spectra also indicate the correlation between H1', H2' and H1' with C1', C2' and C16', respectively. A similar phenomenon can also be found on H3 and H13 which are correlated with C3 and C13.

The aromatic carbons in all compounds were established via the connectivities between the carbon and its neighboring proton by HMBC correlation spectra (Table 3). The aliphatic protons for all title compounds exhibit no correlation with any aromatic carbon. However, the HMBC spectra of ligand **1e** (Fig. 3) has shown that the H4 or H5 is correlated with the carbons C17 and C6 or C7 with

Table 6

Phase transition temperature (°C) and associated enthalpies (kJ mol $^{-1}$) of Cu(II) complexes **2a–2j**.

Complexes		K_1		K_2		SmA		Ι
2a	Heating	•	209.4			•	236.7	•
			(45.1)				(7.6)	
2b	Heating	٠	207.8			•	239.0	•
			(50.6)				(9.7)	
2c	Heating	•	183.8			•	237.5	•
			(39.2)				(10.3)	
2d	Heating	•	125.9	•	179.5	•	233.0	•
			(14.3)		(36.1)		(10.5)	
2e	Heating	•	130.1	٠	171.4	•	225.7	•
			(20.0)		(22.9)		(11.6)	
2f	Heating	•	253.7			•	261.3ª	•
			(31.9)					
2g	Heating	•	241.1			•	250.2ª	•
			(42.4)					
2h	Heating	•	220.5			•	239.8ª	•
			(41.8)					
2i	Heating	•	208.9			•	237.8	•
			(45.0)				(9.0)	
2j	Heating	•	191.3			•	239.2	٠
			(38.7)				(7.9)	

K, crystal; N, nematic; Sm A, smectic A; I; isotropic.

^a Denotes transition temperature derived from unresolved peaks.

Table 7

Phase transition temperatures (°C) and associated enthalpies (kJ mol⁻¹) of Ni(II) complexes **3a-3e**.

Complexes		K ₁		K ₂		K3		Ι
3a	Heating	•	145.4	•			263.9	•
			(23.5)				(47.8)	
3b	Heating	•	133.6	•			244.9	•
			(21.4)				(43.8)	
3c	Heating	•	135.8	•			229.5	•
			(16.5)				(40.1)	
3d	Heating	•	124.8	•	155.4	•	221.7 ^a	•
			(24.5)		(34.5)			
3e	Heating	•	108.6	•	112.9	•	213.9	•
	-		(21.3)		(23.1)		(19.1)	

K, crystal; N, nematic; Sm A, smectic A; I; isotropic.

^a Denotes transition temperature derived from unresolved peaks.

²J. A similar phenomenon can also be found on H6 or H7 which is correlated with C18 and C4 or C5 with ²J. The H8 or H9 is also correlated with carbons C19, C10 or C11 with ²J and C12 with ³J long range connectivities. Similarly, H3 is correlated with C1 and C16 with ²J. The H13 and C16 are correlated with ²J long range conductivities. HMBC spectra also show the correlation between H13 with C14 and C3 with the ³J long range connectivities. The HMBC spectra show that H1 and H2 are correlated with C3, C14, C15 with ²J and C16 with ³J long range connectivities. The emergence of the cross peaks associated with the correlations of C1', C2' and C16' with respective H1', H2' and H16' has confirmed the presence of carbon nuclei from the aliphatic chain.

The ¹H NMR spectra for Cu(II) and Ni(II) complexes display only broad alkoxy signals. All other proton signals close to the paramagnetic Cu(II) and Ni(II) centers are not observable [3,22,23].

3.1.2. FT-IR spectral data

It is clearly shown from the FT-IR spectra of ligands **1a–1j** that they exhibit similar pattern of FT-IR spectra. A strong band observed at 1625 cm⁻¹ corresponds to the stretching of azomethine, C=N group [3,24,25]. A strong band at 2953–2849 cm⁻¹ can be assigned to the stretching vibration of C-H bond from alkoxy chain. The band with strong intensity in the spectra at the range of 1192–1194 cm⁻¹ (C-O) can be ascribed to the ether group [26]. Whereas, the stretching of phenolic C-O at 1282–1285 cm⁻¹ is observed as a medium band [27]. A weak band that is observed at the frequency range of 1471–1473 cm⁻¹ is assignable to the stretching vibration of azo linkages, N=N [28]. Two bands which appear at respective frequency of

Ligands 1a-1j:
1a,1b, 1f-1j (n=5 to n=11)
$K \Longrightarrow SmA \Longrightarrow N \Longrightarrow I$
1c,1d and 1e (n=12,14,16)
$K \Longrightarrow SmA \Longrightarrow I$
<u>Cu(II)</u> Complexes 2a-2j (n=5-12, 14, 16):
$K \Longrightarrow SmA \Longrightarrow I$
Ni(II) Complexes, 3a-3e:
K 🚤 I

K, Crystal; SmA, Smectic A; N, Nematic; I, Isotropic.

Fig. 4. Mesomorphic phase of ligands **1a–1j**, Cu(II) complexes **2a–2j** and phase transition temperature of Ni(II) complexes **3a–3e**.



K, crystal; SmA, Smectic A; N, Nematic; I, Isotropic; CP, Clearing point

Fig. 5. A plot of phase transition temperature upon heating versus the number of carbon atoms in alkoxy chain for the ligands 1a-1j, L (solid line) and their copper(II) complexes, CuL2 (dotted line).



Fig. 6. X-ray pattern of SmA phase of ligand 1a.

1591 cm⁻¹ and 1571 cm⁻¹ can be attributed to the C=C stretching in phenyl ring [29]. The broad band at 3114–3714 cm⁻¹ can be assigned to the stretching frequency of O–H group.

FT-IR spectra data for metal complexes **2a–2j** and **3a–3e** show the similar vibration frequency. The strong band observed at $1610-1611 \text{ cm}^{-1}$ corresponds to the stretching of azomethine, C=N. The reduction of C=N frequency as compared with free ligands suggests the coordination of N atom from the ligand to the central metal atom [22,24,5,30,31]. On the other hand, the disappearance of the O—H band of free ligands in the Ni(II) and Cu(II) metal complexes indicates that OH group is deprotonated and then it is coordinated to the metal ion [22,24,29,5,30]. Furthermore, the coordination of oxygen to metal ion is further confirmed by the stretching vibration of phenolic C—O shifted to higher frequency at $1311-1313 \text{ cm}^{-1}$ for Cu(II) and Ni(II) complexes [27,32]. The other major bands observed at $2921-2850 \text{ cm}^{-1}$ can be assigned to the stretching frequency for C—H bond from alkoxy chain. The band with strong intensity in the spectra at the range of $1206-1200 \text{ cm}^{-1}$ is assignable to the stretching of the C—O ether group. Besides, the weak stretching frequency of azo linkages, N=N is observed at $1470-1471 \text{ cm}^{-1}$ [28] which is similar to the stretching vibration of the uncoordinated ligands. This observation shows that N atom of azo linkages is not coordinated to the Cu(II) metal ion. The stretching frequency for the coordination bonds M—N and M—O in the fingerprint area are too weak and difficult to be identified.

3.2. Mesomorphic behavior

All ligands and their Cu(II) complexes are enantiotropic as revealed by DSC and polarizing optical microscope. The transitions temperatures and associated enthalpies $(kJ mol^{-1})$ of the ligands **1a–1e** and their corresponding Cu(II) and Ni(II) complexes are shown in Tables 5–7, respectively. All the Cu(II) complexes exhibit smetic A (SmA) phase due to the appearance of nematic phase with schlieren texture followed by SmA phase characterized by well defined focal conic fan shape texture in the ligands with *n*-octyloxy and *n*-decyloxy flexible chains. However, all Ni(II) complexes of this series do not exhibit mesomorphic properties. This can be inferred from the observation wherein the Ni(II) experienced the direct isotropization upon heating and cooling without showing the



Fig. 7. Dependence between thickness of the layer in SmA phase and the length of alkoxyl chain for ligands 1a-1e (solid line) and their corresponding Cu(II) complexes 2a-2e (dotted line).



Fig. 8. Schematic drawing of local arrangement of molecules for Cu(II) complexes, 2a-2e.

mesophase. Fig. 4 shows the summary of mesomorphic phase for ligands and their Cu(II) and Ni(II) complexes.

In conventional organic liquid crystal, the intention is to increase intermolecular contact to induce the mesomorphic properties. As for the coordination compound, it is to avoid intermolecular contacts and strong dipolar interaction that are sufficiently strong to cause three-dimensional order in the formation of mesophase [1,24]. Due to the difference of coordination geometry between nickel and copper complexes, the magnitude of intermolecular interaction in copper complexes is also different from nickel complexes. Thus, this shows that the absence of mesophase in Ni(II) complexes can be attributed by the different coordination geometry between Ni(II) and Cu(II) complexes [3,24]. The crystal data in Section 3.5 shows the square planar geometry of Cu(II) complex 2f. Thus, it is suggested that the other homologous member of Cu(II) complexes have the similar geometrical shape as Cu(II) complex 2f. The square planar geometry of Cu(II) complexes can increase the geometrical anisotropy of molecules and is favorable for meso-

Empirical formula	$C_{48}H_{48}CuN_6O_4$
Formula weight	836.49
Crystal color, habit	Orange, prism
Crystal dimensions	$0.520 \times 0.380 \times 0.060$ mm
Crystal system	Monoclinic
Lattice type	C-centered
Lattice parameters	a = 51.044(3) Å
	b = 10.5834(6) Å
	c = 7.7308(5) Å
	$\beta = 94.993(4)^{\circ}$
	$V = 4160.5(5) Å^3$
Space group	C2/c (#15)
Z value	4
D _{calc}	1.335 g/cm ³
F ₀₀₀	1756.00
$\mu(Mo K\alpha)$	5.778 cm^{-1}

phase formation [3]. Whereas, all the Ni(II) complexes **3a–3e** have the inclination toward tetrahedral geometry [3]. This is evident from the ¹H NMR of paramagnetic Ni(II) complexes **3a–3e** which shows only broad signals from the alkoxy chains [33]. The tetrahedral geometry of Ni(II) and crossed alignment of the coordinated ligands are unfavorable for mesophase formation [3]. All the Ni(II) complexes exhibiting mesophase properties are diamagnetic, which have been interpreted to indicate a square planar coordination about the metal [23]. Tuning the molecular geometries is important to achieve a balance in the magnitude of molecular interaction as it optimizes the mesomorphic behavior [24].

3.2.1. Chemical structure-mesormorphic relationship

In order to rationalize the importance of different cored system resulted from the mesormorphic and thermal properties of Cu(II) complexes, the present azobenzene-cored Cu(II) complexes 2a-**2b** and **2h–2i** (**A**) are compared with fluorenes-cored (**B**), biphenyls-cored (C) and stilbenes-cored (D) Cu(II) complexes synthesized by Reddy and co-worker in 1991 [34]. The general molecular structure for these four different core complexes are shown below. It can be noticed that Cu(II) complexes A exhibit enantiotropic SmA phase and thermally stable up to clearing temperature in the range of 33–261 °C. Thus, comparison between the mesophase of Cu(II) complexes A with B, C and D reveal that all the Cu(II) complexes **B**, **C** and **D** also exhibit enantiotropic SmA phase, but with the exception for terminal alkoxyl chain n = 5. Besides, the clearing temperature for Cu(II) complexes **B**, **C** and **D** are in the range of 240-260 °C, 250-278 °C and 272-277 °C, respectively. Thus, the clearing temperatures can be arranged in the increasing order of **A** < **B** < **C** < **D**. Therefore, these observations deduced that the introduction of azobenzene cored can induce the formation of mesophase in lower homologous member of Cu(II) complexes, n = 5 and lower the clearing temperature of the complexes.





Fig. 9. The molecular structure with atom-numbering scheme of Cu(II) complex 2f.



Fig. 10. The molecular packing of Cu(II) complex 2f.

The azobenzene-cored Cu(II) complexes **2a–2j** are also used to make a comparison with azobenzene-cored Cu(II) complexes synthesized by Khandar and Rezvani in 1998 [35]. The general molecular structure of the ligands for the reported Cu(II) complexes synthesized by Khandar and Rezvani are shown below. To ensure that the comparison is relevant, only complexes with m = 5, 6 and 7 are chosen to make a comparison with Cu(II) complexes **2f–2h** (n = 5, 6, 7).



4a (m = 5), **4b** (m = 6), **4c** (m = 7)

Table 9

Summary of intensity measurements for Cu(II) complexes 2f.

Diffractometer	Saturn70		
Radiation	Mo Kα (λ = 0.71070 Å) graphite		
	monochromated		
Voltage, current	50 kV, 100 mA		
Temperature	−159.8 °C		
Detector aperture	$70 \times 70 \text{ mm}$		
Data images	720 exposures		
ω Oscillation range	-110.0° to 70.0°		
Exposure rate	128.0 s/°		
Detector swing angle	-20.05°		
ω Oscillation range	-110.0° to 70.0°		
Exposure rate	128.0 s/°		
Detector swing angle	-20.05°		
Detector position	45.32 mm		
Pixel size	0.137 mm		
$2\theta_{\rm max}$	55.0°		
No. of reflections measured	Total: 15,291		
	Unique: 4708 (<i>R</i> _{int} = 0.0411)		
Corrections	Lorentz-polarization absorption		
	(trans. factors: 0.462-0.966)		

Table 10	
----------	--

Summary of str	ucture solution an	d refinement for	Cu(II)	complexes 2f
Summary of Str	acture solution un	a remement io	cu(II)	complexes 21 .

•	
Structure solution	Direct methods
Refinement	Full-matrix least-squares on F ²
Function minimized	$\Sigma w (F_0^2 - F_c^2)^2$
Least squares weights	$w = 1/[\sigma^2(F_o^2) + (0.0917 \cdot P)^2 + 5.2142 \cdot P],$
	where $P = (Max(F_o^2, 0) + 2F_c^2)/3$
$2\theta_{\max}$ cutoff	55.0°
Anomalous dispersion	All non-hydrogen atoms
No. observations (all reflections)	4708
No. variables	269
Reflection/parameter ratio	17.50
Residuals: R_1 ($I > 2.00\sigma(I)$)	0.0621
Residuals: R (all reflections)	0.0762
Residuals: wR ₂ (all reflections)	0.1801
Goodness of fit indicator	1.114
Max shift/error in final cycle	0.000
Maximum peak in final diff. map	1.23 e ⁻ /Å ³
Minimum peak in final diff. map	$-1.02 \text{ e}^{-}/\text{Å}^{3}$

Table 11				
Atomic coordinates	and	B_{iso}/B_{ea}	and	occupancy.

Atom	x	у	Z	Beq	occ
Cu1	0.2500	0.2500	0.5000	1.35(2)	1/2
01	0.22310(4)	0.2129(2)	0.3230(3)	1.66(4)	1
02	0.15814(4)	0.3910(2)	-0.0879(3)	1.94(4)	1
N1	0.22688(4)	0.1767(2)	0.6743(3)	1.44(4)	1
N2	0.11497(8)	0.0958(4)	0.5991(4)	4.81(9)	1
N3	0.10550(10)	0.1811(4)	0.5319(5)	5.58(10)	1
C1	0.23711(5)	0.1353(3)	0.8249(4)	1.43(5)	1
C2	0.26410(5)	0.1396(3)	0.8890(4)	1.30(4)	1
C3	0.22806(5)	0.4309(3)	-0.0401(4)	1.54(5)	1
C4	0.20222(5)	0.4375(3)	-0.1050(4)	1.67(5)	1
C5	0.18331(5)	0.3694(3)	-0.0216(4)	1.58(5)	1
C6	0.19045(5)	0.2913(3)	0.1170(4)	1.63(5)	1
C7	0.21696(5)	0.2859(3)	0.1888(4)	1.45(5)	1
C8	0.13701(6)	0.3341(4)	-0.0053(4)	2.27(6)	1
C9	0.11175(6)	0.3896(4)	-0.0877(5)	2.49(6)	1
C10	0.08768(6)	0.3396(4)	-0.0090(5)	3.17(7)	1
C11	0.06233(7)	0.3962(5)	-0.0908(7)	4.38(9)	1
C12	0.03788(7)	0.3501(6)	-0.0129(7)	5.78(13)	1
C13	0.19924(5)	0.1577(3)	0.6403(4)	1.60(5)	1
C14	0.18371(6)	0.2550(3)	0.5633(4)	1.85(6)	1
C15	0.15671(7)	0.2431(4)	0.5416(5)	2.57(7)	1
C16	0.14476(6)	0.1321(4)	0.5948(4)	2.99(7)	1
C17	0.16008(6)	0.0342(4)	0.6665(4)	2.62(6)	1
C18	0.18729(6)	0.0460(3)	0.6872(4)	1.99(5)	1
C19	0.07526(8)	0.1512(6)	0.5471(7)	5.58(13)	1
C20	0.05928(10)	0.2347(6)	0.4572(10)	6.0(2)	1
C21	0.03277(9)	0.2279(5)	0.4686(8)	4.95(11)	1
C22	0.02183(7)	0.1348(5)	0.5643(5)	3.69(8)	1
C23	0.03771(8)	0.0470(6)	0.6512(6)	4.68(10)	1
C24	0.06522(8)	0.0548(6)	0.6445(6)	5.59(13)	1

 $B_{\rm eq} = 8/3\pi^2 (U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos\gamma + 2U_{13}(aa^*cc^*)\cos\beta + 2U_{23}(bb^*cc^*)\cos\alpha.$

Comparison in terms of mesomorphic properties between Cu(II) complexes derived from ligands **4a–4c** and the presence of the Cu(II) complexes **2f–2h** reveal that the difference are pronounced. Cu(II) complexes **2f–2h** exhibit enantiotropic SmA phase during heating and cooling process. Whilst only Cu(II) complexes derived from ligand **4b** show a monotropic SmA phase during cooling process. On the other hand, optical observation also reveals that the SmA phase for Cu(II) complexes derived from ligand **4b** exhibits different size of "Maltese Crosses" texture. These observation are

Table 12

Atom	x	у	z	B _{iso}	occ
H1	0.2253	0.0986	0.8990	1.71	1
H3	0.2410	0.4746	-0.0981	1.84	1
H4	0.1972	0.4873	-0.2046	2.00	1
H6	0.1775	0.2406	0.1649	1.95	1
H8A	0.1389	0.3523	0.1208	2.72	1
H8B	0.1371	0.2414	-0.0217	2.72	1
H9A	0.1102	0.3703	-0.2135	2.98	1
H9B	0.1124	0.4826	-0.0745	2.98	1
H10A	0.0893	0.3582	0.1170	3.80	1
H10B	0.0870	0.2466	-0.0232	3.80	1
H11A	0.0633	0.4892	-0.0789	5.26	1
H11B	0.0607	0.3762	-0.2163	5.26	1
H12A	0.0382	0.3785	0.1080	6.94	1
H12B	0.0373	0.2576	-0.0168	6.94	1
H12C	0.0223	0.3845	-0.0794	6.94	1
H14	0.1918	0.3297	0.5257	2.23	1
H15	0.1462	0.3099	0.4907	3.08	1
H17	0.1520	-0.0412	0.7017	3.14	1
H18	0.1978	-0.0223	0.7333	2.38	1
H20	0.0664	0.2973	0.3868	7.20	1
H21	0.0216	0.2887	0.4093	5.94	1
H22	0.0033	0.1315	0.5698	4.42	1
H23	0.0303	-0.0184	0.7155	5.62	1
H24	0.0766	-0.0044	0.7051	6.71	1

different from the existence of SmA phase with focal conic fan shape texture for Cu(II) complexes **2f–2h**. Besides, the isotropization temperature of Cu(II) complexes **2f–2h** are found to be significantly higher than those complexes derived from ligands **4a–4b**.

3.3. The influence of molecular structure on thermal stability

A distinct odd–even effect of the clearing temperature of ligands **1a–1f** is illustrated in Fig. 5. The values of clearing temperature tend to decrease in a regular, zig-zag fashion with the number of carbon atoms in alkoxy chain (*n*) ranges from n = 5 to n = 12. However, the odd–even effect becomes less distinctive when the number of carbon in the alkoxyl chain, *n* is larger than 8. This is due to the increase in flexibility of the terminal alkoxyl chain [36–38]. These observations strongly show that ligands with even number of terminal alkoxy chain have higher clearing point than those with odd numbers. Such pattern of regular change often been observed in compounds consisting of central mesogenic structure having variable lengths of terminal alkyl chain [38–40].

Generally, the odd–even effect can be explained from a consideration of molecular structure. Homologous with the even member alkoxy chain exhibits colinearity to the rigid core segment in the preferred *trans* conformation geometry [36,37]. On the other hand, the odd member alkoxy chain shows non-colinearity to the rigid core segment [36,37]. The presence of alkoxyl groups of even parity at the terminal are 'in line' with the molecular long axis and therefore enhance the molecular anisotropic and result in high clearing temperature, whereas the odd numbers have the opposite effect [36,37].

From Fig. 5, a general trend can be noted. The transition temperatures for all the Cu(II) complexes are significantly higher than those of the free ligands and decrease as the number of carbon atoms in flexible alkoxy chain increases. This is due to the significant higher molecular weight upon complexation and the increasing number of interacting site [3]. Besides, the clearing temperatures of Cu(II) complexes increase by 60–70 °C upon complexation indicate that the introduction of metal atom increases the isotropic temperature of the corresponding ligands. These phenomena can be associated with the thermal stability upon coordination.

3.4. X-ray diffraction study on smectic A phase for ligands **1a–1e** and Cu(II) complexes **2a–2e**

In order to investigate the liquid crystalline structure of obtained materials the X-ray studies have been carried out for aligned samples. Ligands **1a-1e** and their corresponding Cu(II) complexes 2a-2e show mesomorphism with SmA phase below isotropic phase as confirmed by X-ray diffraction, thus they show similar X-ray patterns. Low angle Bragg reflections further confirmed the existence of layers (Fig. 6). The diffused signal at equatorial position reflects the lack of molecular long range order inside each smectic layer or the lateral distribution of the molecules within each layer is in random manner. For ligands 1a-1e the layer spacing increases by 1.25 Å (Fig. 7) with the elongation of alkoxyl chain length by one carbon atom. However for their corresponding Cu(II) complexes 2a-2e, the layer spacing increases only by 1.04 Å (Fig. 7). The layer spacing for the ligands corresponds well to their molecular length while the layer thickness of the complexes is significantly smaller as compared to their molecular length. This show the presences of some interdigitation of molecular alkoxy chains between neighboring layers. The presences of the intercalated structure is resulted due to the molecular shape. The complex molecule has tri-cylindrical shape (Fig. 8) with a much larger cross section for the mesogenic core than the molecular tails when it rotate. This shows the contrary between the tri-cylindrical shape with the rod-like ligands. In order to fill the space efficiently the

Table 13	
A	41.001.000

Anisotropic	displacement	parameters.

Table 14	
Bond lengths	(Å).

Atom	Atom	Distance	Atom	Atom	Distance
Cu1	01	1.8932(19)	Cu1	01 ¹	1.8932(19)
Cu1	N1	2.022(3)	Cu1	N1 ¹	2.022(3)
01	C7	1.309(4)	02	C5	1.360(4)
02	C8	1.433(4)	N1	C1	1.309(4)
N1	C13	1.427(4)	N2	N3	1.129(6)
N2	C16	1.572(6)	N3	C19	1.590(7)
C1	C2	1.424(4)	C2	C3 ¹	1.415(4)
C2	C71	1.421(4)	C3	C4	1.371(4)
C4	C5	1.405(4)	C5	C6	1.378(4)
C6	C7	1.418(4)	C8	C9	1.507(5)
C9	C10	1.513(5)	C10	C1	1.513(5)
C11	C12	1.513(6)	C13	C14	1.400(4)
C13	C18	1.393(5)	C14	C15	1.380(5)
C15	C16	1.402(6)	C16	C17	1.384(5)
C17	C18	1.390(5)	C19	C20	1.353(8)
C19	C24	1.392(8)	C20	C21	1.366(7)
C21	C22	1.380(7)	C22	C23	1.370(7)
C23	C24	1.412(6)			

Symmetry operators: (1) -x + 1/2, -y + 1/2, -z + 1.

molecules interdigitate their tails when they are packed into layers.

3.5. Crystal structure of Cu(II) complex 2f

The molecular structure with the atom-numbering scheme and packing of Cu(II) complex **2f** are shown in Figs. 9 and 10, respectively. Crystal data, intensity measurement and structure solution and refinement of Cu(II) complexes are collated in Tables 8–10, respectively. The atomic coordinates, $B_{\rm iso}/B_{\rm eq}$, $B_{\rm iso}$ involving hydrogen atoms and anisotropic displacement parameter are given in Tables 11–13, respectively. Tables 14 and 15 show the selected bond lengths and bond angles whereas Tables 16 and 17 show the bond lengths and bond angles involving hydrogen.

Atom	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Cu1	0.0190(3)	0.0183(3)	0.0137(3)	-0.0013(2)	0.0002(2)	0.0015(2)
01	0.0226(10)	0.0243(10)	0.0162(10)	-0.0028(8)	0.0005(8)	0.0028(8)
02	0.0207(10)	0.0301(11)	0.0225(10)	0.0027(9)	-0.0017(8)	0.0018(9)
N1	0.0207(11)	0.0170(11)	0.0172(11)	0.0013(9)	0.0028(9)	-0.0002(9)
N2	0.107(4)	0.041(2)	0.031(2)	0.028(2)	-0.016(2)	-0.006(2)
N3	0.137(4)	0.036(2)	0.044(2)	-0.007(3)	0.033(3)	0.002(2)
C1	0.025(2)	0.0141(13)	0.0155(12)	-0.0008(10)	0.0046(10)	-0.0026(10)
C2	0.0207(13)	0.0148(12)	0.0141(12)	0.0013(10)	0.0028(10)	-0.0013(10)
C3	0.025(2)	0.0167(13)	0.0165(13)	-0.0001(10)	0.0021(11)	0.0007(11)
C4	0.026(2)	0.020(2)	0.0173(13)	0.0005(11)	-0.0010(11)	0.0011(11)
C5	0.0205(13)	0.022(2)	0.0170(13)	0.0010(11)	-0.0009(10)	-0.0051(11)
C6	0.024(2)	0.021(2)	0.0169(13)	-0.0022(11)	0.0034(11)	-0.0014(11)
C7	0.025(2)	0.0182(13)	0.0120(12)	0.0023(11)	-0.0001(10)	-0.0032(11)
C8	0.025(2)	0.036(2)	0.025(2)	-0.0019(13)	0.0001(12)	0.0013(13)
C9	0.024(2)	0.034(2)	0.036(2)	0.0014(13)	0.0003(13)	-0.002(2)
C10	0.022(2)	0.061(3)	0.037(2)	-0.006(2)	-0.001(2)	-0.001(2)
C11	0.022(2)	0.066(3)	0.079(3)	0.006(2)	0.006(2)	0.000(3)
C12	0.023(2)	0.129(5)	0.067(3)	-0.012(3)	0.001(2)	-0.003(3)
C13	0.0175(13)	0.028(2)	0.0157(12)	0.0013(11)	0.0036(10)	-0.0034(11)
C14	0.025(2)	0.028(2)	0.017(2)	0.0055(11)	-0.0000(12)	-0.0034(11)
C15	0.027(2)	0.049(3)	0.021(2)	0.0162(13)	-0.0034(13)	-0.0113(13)
C16	0.022(2)	0.065(3)	0.027(2)	-0.001(2)	0.0040(13)	-0.014(2)
C17	0.026(2)	0.048(2)	0.026(2)	-0.010(2)	0.0053(12)	-0.009(2)
C18	0.026(2)	0.028(2)	0.021(2)	-0.0034(12)	0.0036(11)	-0.0021(12)
C19	0.035(3)	0.123(5)	0.058(3)	-0.030(3)	0.022(2)	-0.043(3)
C20	0.033(3)	0.089(4)	0.110(5)	-0.015(3)	0.027(3)	-0.009(4)
C21	0.035(3)	0.072(3)	0.084(4)	-0.008(2)	0.021(3)	0.000(3)
C22	0.020(2)	0.071(3)	0.049(3)	-0.001(2)	0.007(2)	-0.003(2)
C23	0.036(2)	0.095(4)	0.049(3)	0.011(3)	0.010(2)	0.009(3)
C24	0.039(3)	0.126(5)	0.045(3)	0.032(3)	-0.010(2)	-0.018(3)

Table 15 Bond angles (°)

0							
Atom	Atom	Atom	Angle	Atom	Atom	Atom	Angle
01	Cu1	01 ¹	180.00(13)	01	Cu1	N1	88.48(9)
01	Cu1	$N1^1$	91.52(9)	01 ¹	Cu1	N1	91.52(9)
01 ¹	Cu1	$N1^1$	88.48(9)	N1	Cu1	$N1^1$	180.00(12)
Cu1	01	C7	123.99(18)	C5	02	C8	119.0(3)
Cu1	N1	C1	120.68(18)	Cu1	N1	C13	123.81(17)
C1	N1	C13	115.4(3)	N3	Ν	C16	99.8(4)
N2	N3	C19	100.7(5)	N1	C1	C2	126.7(3)
C1	C2	C31	117.8(3)	C1	C2	C71	123.0(3)
C31	C2	C71	119.2(3)	C21	C3	C4	121.5(3)
C3	C4	C5	118.9(3)	02	C5	C4	113.9(3)
02	C5	C6	124.8(3)	C4	C5	C6	121.3(3)
C5	C6	C7	120.5(3)	01	C7	$C2^1$	122.5(3)
01	C7	C6	119.2(3)	$C2^1$	C7	C6	118.3(3)
02	C8	C9	107.3(3)	C8	C9	C10	112.9(3)
C9	C10	C11	112.8(4)	C10	C11	C12	114.3(4)
N1	C13	C14	119.3(3)	N1	C13	C18	121.3(3)
C14	C13	C18	119.3(3)	C13	C14	C15	120.5(3)
C14	C15	C16	119.7(3)	N2	C16	C15	131.1(4)
N2	C16	C17	108.8(3)	C15	C16	C17	120.0(3)
C16	C17	C18	120.2(4)	C13	C18	C17	120.1(3)
N3	C19	C20	112.2(5)	N3	C19	C24	126.3(4)
C20	C19	C24	121.5(5)	C19	C20	C21	119.3(6)
C20	C21	C22	121.4(5)	C21	C22	C23	119.9(4)
C22	C23	C24	119.4(5)	C19	C24	C23	118.5(5)

Symmetry operators: (1) -x + 1/2, -y + 1/2, -z + 1.

 Table 16

 Bond lengths involving hydrogens (Å).

Atom	Atom	Distance	Atom	Atom	Distance	
C1	H1	0.950	C3	H3	0.950	
C4	H4	0.950	C6	H6	0.950	
C8	H8A	0.990	C8	H8B	0.990	
C9	H9A	0.990	C9	H9B	0.990	
C10	H10A	0.990	C10	H10B	0.990	
C11	H11A	0.990	C11	H11B	0.990	
C12	H12A	0.980	C12	H12B	0.980	
C12	H12C	0.980	C14	H14	0.950	
C15	H15	0.950	C17	H17	0.950	
C18	H18	0.950	C20	H20	0.950	
C21	H21	0.950	C22	H22	0.950	
C23	H23	0.950	C24	H24	0.950	

Fig. 10 shows the discrete molecule of Cu(II) complex **2f** consisting of two ligands coordinated to one Cu(II) metal. This crystal structure further confirmed that the azo moties does not involve in coordination which is in agreement with FTIR spectra and elemental analysis data.

The Cu(II) complexes crystalline into C-centered monoclinic cell with a space group C2/*c* with unit cell paraneters *a* = 51.0443(3) Å, *b* = 10.5834(6) Å, β = 94.993(4)°, *V* = 4160.5(5) Å³. Table 12 shows that the cisoid angles of N1–Cu–O1 and O1*–Cu–N1 are 91.52° and 88.48°, respectively. While both the transoid angles of O1*–Cu–O1 and N1*–Cu–N1 are 180°. The cisoid and transoid angles show that the ligands have an approximately square planar configuration around the Cu center ion. The cisoid and transoid angles are similar to the corresponding value reported by Ünvera and Hayvalib which were 91,48°, 88.52° and 180° for copper(II) complexes derived from 2-[(Z)-[furan-2-ylmethyl]imino]methyl]-6-methoxyphenol [42]. Besides, these observations are similar to the value (91.62°, 88.38° and 180°) reported by Mandal and Rout for bis(*N*-2-hydroxybenzyl-2-furylmethylimine)copper(II) [41].

The bond lengths of Cu—N1(2.022 Å) and Cu—O1(1.893 Å) are similar to the values reported by Ünvera and Hayvalib which were

Table 17		
Bond angles	involving hydrogens	(°).

Atom	Atom	Atom	Angle	Atom	Atom	Atom	Angle
N1	C1	H1	117	C2	C1	H1	117
$C2^1$	C3	H3	119	C4	C3	H3	119
C3	C4	H4	121	C5	C4	H4	121
C5	C6	H6	120	C7	C6	H6	120
02	C8	H8A	110	02	C8	H8B	110
C9	C8	H8A	110	C9	C8	H8B	110
H8A	C8	H8B	109	C8	C9	H9A	109
C8	C9	H9B	109	C10	C9	H9A	109
C10	C9	H9B	109	H9A	C9	H9B	108
C9	C10	H10A	109	C9	C10	H10B	109
C11	C10	H10A	109	C11	C10	H10B	109
H10A	C10	H10B	108	C10	C11	H11A	109
C10	C11	H11B	109	C12	C11	H11A	109
C12	C11	H11B	109	H11A	C11	H11B	108
C11	C12	H12A	109	C11	C12	H12B	109
C11	C12	H12C	109	H12A	C12	H12B	109
H12A	C12	H12C	109	H12B	C12	H12C	109
C13	C14	H14	120	C15	C14	H14	120
C14	C15	H15	120	C16	C15	H15	120
C16	C17	H17	120	C18	C17	H17	120
C13	C18	H18	120	C17	C18	H18	120
C19	C20	H20	120	C21	C20	H20	120
C20	C21	H21	119	C22	C21	H21	119
C21	C22	H22	120	C23	C22	H22	120
C22	C23	H23	120	C24	C23	H23	120
C19	C24	H24	121	C23	C24	H24	121

Symmetry operators: (1) -x + 1/2, -y + 1/2, -z.

2.006 (Cu—N) and 1.893 (Cu—O) for copper(II) complexes derived from 2-[(Z)-[furan-2-ylmethyl]imino]methyl]-6-methoxyphenol [42]. The elongated Cu—N bonds have also been observed for other Schiff base complexes [41]. Thus, the Cu(II) complex of **2f** can also be described as distorted square planar geometries as evident from the Cu—N1(2.022 Å) bond being slightly longer than the corresponding Cu—O1(1.893 Å) bond.

4. Conclusion

Two new series of Cu(II) and Ni(II) complexes derived from 4-(4-alkoxy-2-hydroxybenzylideneamino)azobenzene homologous have been successfully synthesized and characterized by ¹³C NMR, 1D and 2D ¹H NMR. Mesomorphic behavior is found to be controlled by the number of carbon atoms in alkoxy chain (*n*) and nature of central metal ion. All ligands and Cu(II) complexes show liquid crystalline character while all Ni(II) complexes are non-mesomorphic. XRD studies confirmed the existence of SmA phase for ligands and Cu(II) complexes. The X-ray crystallographic confirmed the square planar geometry of bis[4-(4-alkoxy-2hydroxybenzylideneamino)azobenzene]copper(II) complex.

Acknowledgements

The main author (G.-Y. Yeap) would like to thank Universiti Sains Malaysia for the RU Grant No. 1001/PKIMIA/811127 and Incentive Grant No. 1001/PKIMIA/822208.

References

- [1] E. Meyer, C. Zucco, H. Gallarlo, J. Mater. 8 (1998) 1351–1354.
- [2] C.K. Lee, M.C. Ling, J.B. Ivan Lim, J. Chem. Soc. Dalton Trans. (2003) 4731-4737.
- [3] H.W. Chae, O.N. Kadhin, M.G. Choi, J. Liq. Cryst. 36 (2009) 53-60.
- [4] K.P. Huang, T.K. Misra, G.R. Wang, B.Y. Wang, C.Y. Liu, J. Chromatogr. A. 1215 (2008) 177-1845.
- [5] A. Suste, V. Sunjic, Liq. Cryst. 20 (1996) 219–224.
- [6] S. Tantrawong, P. Styring, Liq. Crys. 22 (1997) 17-22.
- [7] C.Y. Liu, J.L. Chen, C.C. Shiue, K.T. Liu, J. Chromatogr. A. 862 (1999) 65-83.

G.-Y. Yeap et al./Journal of Molecular Structure 999 (2011) 68-82

- [8] K.P. Huang, T.K. Misra, G.R. Wang, B.Y. Huang, C.Y. Liu, J. Chromatogr. A 1215 (2008) 177–1845.
- [9] C. Gayathri, A. Ramalingan, Spectrochim. Acta A. 69 (2008) 980-984.
- [10] T. Xu, C. Zhang, Y. Lin, S. Qi, J. Inorg. Chem. 8 (1999) 1367-1372.
- [11] A. Saad, T.V. Galstyan, M.M. Denariez-Roberge, M. Dumont, Opt. Commun. 151 (1998) 235–240.
- [12] J.M. Baena, J. Barbera, P. Espinet, A. Ezcurra, M.B. Ros, J.L. Serrano, J. Am. Chem. Soc. 116 (1994) 1899.
- [13] E. Ispir, Dyes Pigm. 82 (2009) 13-19.
- [14] SIR2008, M.C. Burla, R. Caliandro, M. Camalli, B. Carrozzini, G.L. Cascarano, L. De Caro, C. Giacovazzo, G. Polidori, R. Spagna, 2007.
- [15] D.T. Cromer, J.T. Waber, International Tables for X-ray Crystallography, vol. 4, The Kynoch Press, Birmingham, England, 1974 (Table 2.2 A).
- [16] J.A. Ibers, W.C. Hamilton, Acta Cryst. 17 (1964) 781.
- [17] D.C. Creagh, W.J. McAuley, in: A.J.C. Wilson (Ed.), International Tables for Crystallography, vol. C, Kluwer Academic Publishers, Boston, 1992, pp. 219– 222 (Table 4.2.6.8).
- [18] D.C. Creagh, J.H. Hubbell, International Tables for Crystallography, in: A.J.C. Wilson (Ed.), vol. C, Kluwer Academic Publishers, Boston, 1992, pp. 200–206.
- [19] G.M. Sheldrick, Acta Cryst. A64 (2008) 112-122.
- [20] B.I. Ostrovskii, A.Z. Rabinovich, A.S. Sonic, E.L. Sorkin, B.A. Strukov, S.A. Taraskin, Ferroelectrics 24 (1980) 309.
- [21] H.K. Fun, R. Kia, S. Schiffers, M. Moghadam, P.R. Raithby, Acta Cryst. E64 (2008) 01856-01857.
- [22] Z. Rezvani, B. Divband, A.R. Abbasi, K. Nejati, Polyhedron 25 (2006) 1915– 1920.
- [23] S.A. Hudson, M. Maitlis, Chem. Rev. 93 (1993) 861-885.
- [24] Z. Rezvani, L.R. Ahar, K. Nejati, S.M. Seyedahnadian, Acta Chim. Slov. 51 (2004) 675–686.

- [25] G.Y. Yeap, T.C. Hng, W.A. Kamil Mahmood, M.M. Ito, Y. Youhei, Y. Takanishi, H. Takezoe, Liq. Cryst. 33 (2010) 979–986.
- [26] E. Pretsch, P. Buhlmann, C. Affolter, Structure Determination of Organic Compound, Spring-Verlag, Berlin, Heidelberg, New York, 2000.
- [27] I.M. Mustafaa, M.A. Hapipaha, M.A. Abdullab, T.R. Warda, Polyhedron 28 (2009) 3993–3998.
- [28] G.Y. Yeap, C.H. Ong, D. Takeuchi, M. Kakeya, K. Osakada, W.A.K. Mahmood, O. Atsuko, V. Vill, J. Mol. Struct. 882 (2008) 1–8.
- [29] G.Y. Yeap, A.T. Mohamad, H. Osman, J. Mol. Struct. 982 (2010) 33-44.
- [30] D. Pucci, I. Aiello, A. Bellusci, G. Callipari, A. Crispini, M. Ghedini, Mol. Cryst. Liq.
- Cryst. 500 (2009) 144–154. [31] V.S. Nandiraju, D. Singha, M. Das, M.K. Paul, Mol. Cryst. Liq. Cryst. 373 (2002) 105–117.
- [32] B.S. Creavena, B. Duffa, D.A. Egana, K. Kavanaghc, G. Rosaird, V.R. Thangellaa, M. Walsha, Inorg. Chim. Acta 363 (2010) 4048–4085.
- [33] C.E. Housecroft, A.G. Sharpe, Inorganic Chemistry, third ed., Pearson Education Limited, 2008. pp. 671–672.
- [34] Karuna P. Reddy, T.R. Brown, J. Mater. Chem. 1 (5) (1991) 757-764.
- [35] A.A. Khandar, Z. Rezvani, Polyhedron 18 (1999) 129–133.
- [36] K. Okamato, T. Kawamura, M. Sone, K. Ogino, Liq. Cryst. 9 (2007) 1001-1007.
- [37] J. Van Der Veen, W.H. De Jue, A.H. Grobben, J. Boven, Mol. Cryst. Liq. Cryst. 17
- (1972) 291–301.
- [38] j. Zienkiewicz, Z. Galewski, Liq. Cryst. 23 (1997) 9-16.
- [39] Gray, G.W., Harrison, K.J., 1971. Molecular Theories and Structure.
- [40] A.C. Griffin, T.R. Britt, J. Am. Chem. Soc. 103 (6) (1981) 4957-4959.
- [41] H. Ünvera, Z. Hayvalib, Spectrochim. Acta A: Mol. Biomol. Spectrosc. 75 (2010) 782-788.
- [42] S. Mandal, A.K. Rout, Transit. Met. Chem. 34 (2009) 719-724.