

# Discotic metallomesogens: mesophase crossover of columnar rectangular to hexagonal arrangements in bis(hydrazinato)nickel(II) complexes

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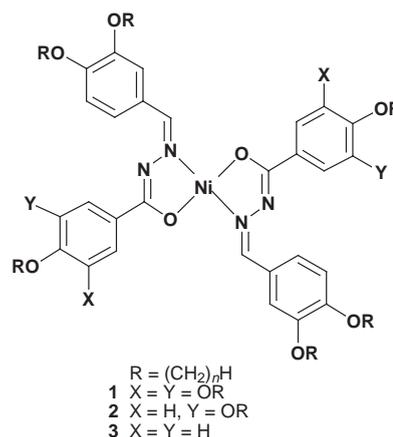
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Three series of *N*-(3,4-dialkoxybenzylidene)-*N'*-(3',4',5'-trialkoxybenzoyl)hydrazine and their nickel(II) complexes, bis[*N*-(3,4-dialkoxybenzylidene)-*N'*-(3',4',5'-trialkoxybenzoyl)hydrazinato]nickel(II), were prepared and characterized. The mesomorphic properties of these disc-like compounds were also studied in terms of liquid crystallinity. The orange nickel(II) complexes with ten soft alkoxy side chains exhibited columnar disordered mesophases, which were characterized based on DSC analysis and optical polarized microscopy. Nickel complexes with shorter side chains ( $n = 5-8$ ) displayed a monotropic columnar rectangular disordered ( $\text{Col}_{\text{rd}}$ ) phase; however, complexes with longer side chains showed monotropic ( $n = 10$ ) and enantiotropic ( $n = 12, 14$ ) columnar hexagonal disordered ( $\text{Col}_{\text{hd}}$ ) phases. Similar nickel complexes ( $n = 14$ ) with eight side chains exhibited a columnar hexagonal phase, whereas complexes ( $n = 14$ ) with six side chains formed crystalline phases. The structures of these columnar disordered phases were confirmed by X-ray powder diffraction. XRD data indicated that mesophase crossover from columnar rectangular ( $\text{Col}_{\text{r}}$ ) to hexagonal arrangements ( $\text{Col}_{\text{h}}$ ) was observed with increasing side chain lengths.

Recently, many disc-like coordination complexes with a central geometry of either square planar (Cu, Ni, Pd) or square pyramidal (VO) structure as the rigid core have been prepared, and these metal complexes have been found to exhibit novel mesomorphic properties.<sup>1</sup> In general this type of metallomesogenic structure was generated by incorporation of single or multiple metal centers<sup>2</sup> into traditional organic molecules. This synthetic strategy has been widely used to design metallomesogenic materials with a variety of geometrical structures and molecular shapes.<sup>1e</sup> The rich electronic and magnetic properties originating from metal centers makes such materials potential candidates<sup>1e,3</sup> for molecular based applications.

Columnar hexagonal and rectangular arrangements are among the two common phases observed among discotic<sup>2e,4,5</sup> molecules. Moreover, certain molecules, which are not themselves disc-shaped,<sup>6</sup> may also exhibit similar columnar phases. A typical monomesomorphic transition<sup>7</sup> of the crystal-to-columnar-to-isotropic ( $\text{K} \rightarrow \text{Col} \rightarrow \text{I}$ ) has often been observed for this type of columnar mesogen; however, discotic molecules with polyomesomorphic properties are relatively rare.<sup>4</sup> Among them mesophase crossover from columnar rectangular to hexagonal arrangements identified by high-resolution X-ray diffraction (XRD) with increasing side chain lengths has been observed in several columnar systems.<sup>4,8</sup> This type of phase transition<sup>9</sup> has generally been attributed to the fact that shorter side chain complexes favored the greater core interaction needed for the formation of  $\text{Col}_{\text{rd}}$  phases. A similar preference of  $\text{Col}_{\text{r}}$  over the  $\text{Col}_{\text{h}}$  phase for larger metal centers, such as  $\text{M} = \text{Pd}$  over the Cu analogue<sup>8a</sup> also occurs in bis( $\beta$ -diketonate) metal complexes.

In this paper, we report the preparation, characterization and mesomorphic properties of a series of nickel(II) complexes 1–3 of *N*-(3,4-dialkoxybenzylidene)-*N'*-(3',4',5'-trialkoxybenzoyl)hydrazine. These disc-like molecules exhibited columnar mesophases as expected. The mesophase crossover of rectangular to hexagonal phase with increasing side chain length was also observed in these nickel(II) complexes. In addition, the effect of side chain density on the formation and/or stability of columnar mesophases was also studied in detail.



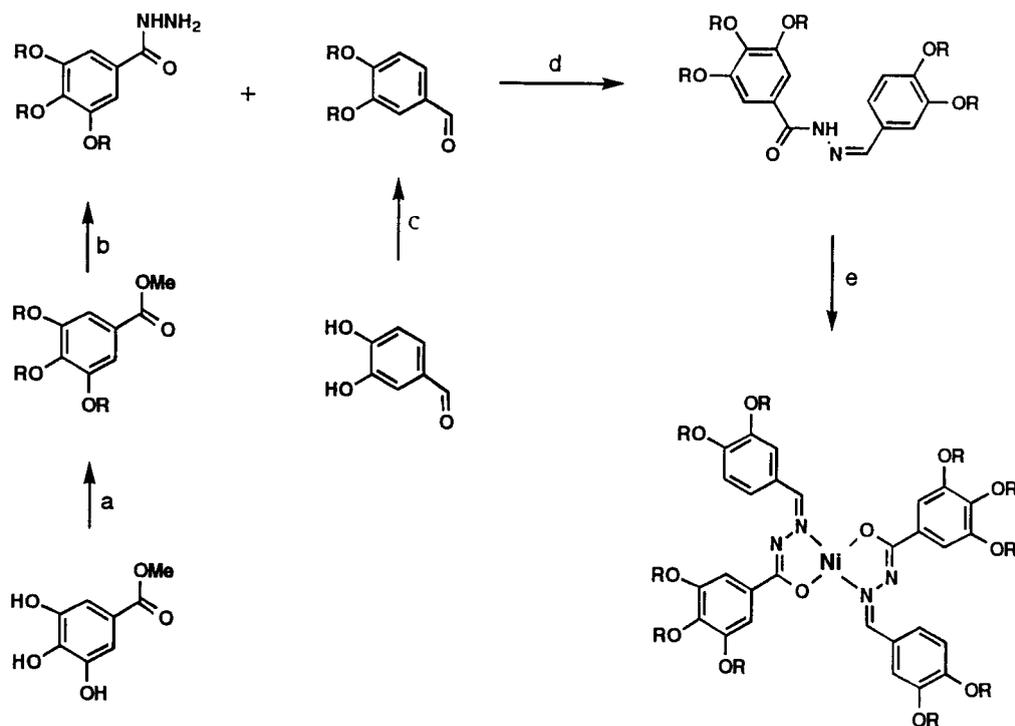
## Results and Discussion

### Synthesis

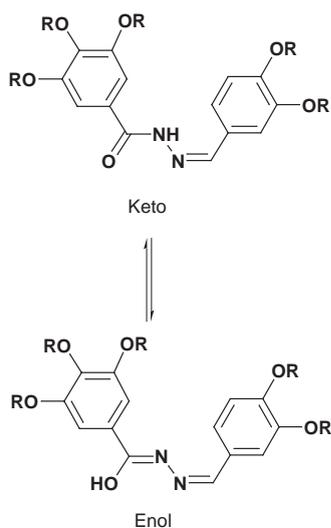
The synthetic procedures for this type of monodentate hydrazone Schiff base<sup>10</sup> are quite straightforward, and summarized in Scheme 1. Reaction of methyl 3,4,5-trialkoxybenzoate esters with hydrazine hydrate in refluxing absolute ethanol gave 3,4,5-trialkoxybenzoylhydrazine as a white solid. The Schiff bases of *N*-(3,4-dialkoxybenzylidene)-*N'*-(3',4',5'-trialkoxybenzoyl)hydrazine were obtained by the condensation reactions of these hydrazine derivatives with 3,4-dialkoxybenzaldehyde in refluxing ethanol. The Schiff bases were isolated by recrystallization from ethanol as light yellow solids.

Aroylhydrazone derivatives<sup>11</sup> exist in two different keto–enol tautomeric forms (Scheme 2). The conjugating ability<sup>12</sup> of the substituents on the ketone moiety was found to influence the ratio of these two isomers. The increasing conjugating ability of aryl substituents preferred the enolic tautomer form.

Two different structural types<sup>10</sup> of nickel(II) complexes could be prepared and isolated depending on the nickel(II) salts used. Reaction of Schiff bases with nickel(II) acetate produced the square planar bis(aroylhydrazinato)nickel(II) complexes; however, the reaction with nickel(II) chloride gave the octahedral



**Scheme 1** Reagents and conditions: (a) RBr (3.0 equiv.),  $K_2CO_3$  (7.0 equiv.), KI (catalyst), refluxing in MeCOMe, 72 h, 73–94%. (b)  $NH_2NH_2$  (1.5 equiv.), refluxing in absolute EtOH, 12 h, 85–90%. (c) RBr (2.0 equiv.),  $K_2CO_3$  (3.0 equiv.), KI, refluxing in MeCOMe, 24 h, 79–88%. (d) Acetic acid (3 drops), refluxing in EtOH, 12 h, 70–75%. (e)  $Ni(OAc)_2$  (1.1 equiv.), refluxing in absolute  $C_2H_5OH$ , 24 h 73–80%.



**Scheme 2**

dichlorobis(aroilylhydrazone)nickel(II) complexes. Dehaloprotection with alcoholic potassium hydroxide converted the octahedral nickel(II) to planar nickel(II) complexes. The preparation of octahedral complexes was not attempted in this work. The square planar nickel(II) complexes studied in this work were prepared by reaction of *N*-(3,4-dialkoxybenzylidene)-*N'*-(3',4',5'-trialkoxybenzoyl)hydrazine with  $Ni(OAc)_2$  in refluxing ethanol. The nickel complexes were then isolated as orange crystals by recrystallization from absolute ethanol in a high yield of 76–86%. All the nickel(II) complexes are diamagnetic, and all display sharp peaks in their  $^1H$  NMR spectra. Elemental analyses also confirmed the identity of the complexes.

### Mesomorphic properties

Mesomorphic studies in columnar systems of metal bis( $\beta$ -diketonates) with various numbers of side chains indicated

that the formation<sup>2d,e,6a</sup> and stability of the columnar phases by disc-like molecules were strongly dependent on the numbers of flexible side chains, *i.e.* side chain density. Increasing the number of side chains often improved the liquid crystalline behavior in this type of metallomesogenic system.

### Complexes with ten side chains

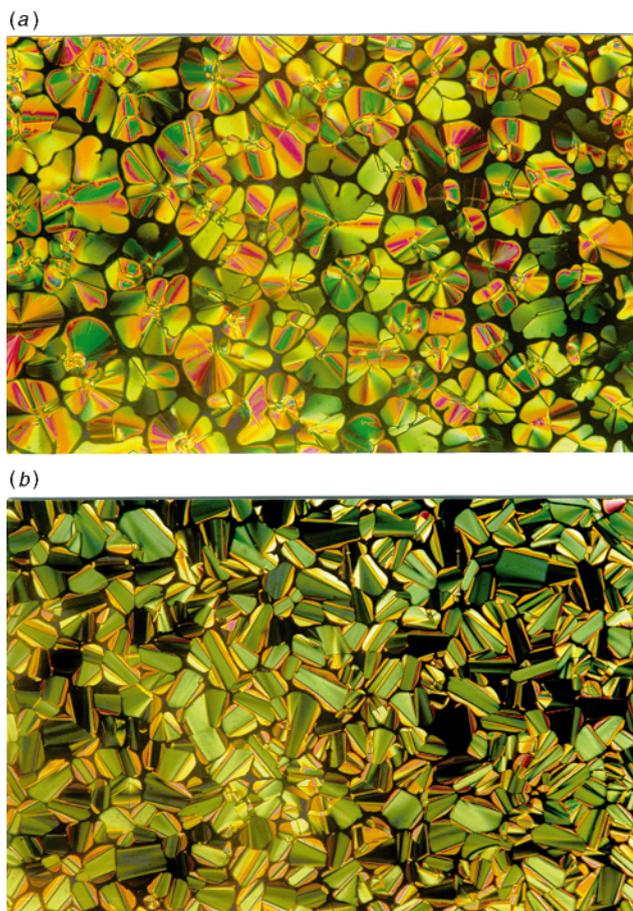
These nickel complexes all exhibited the liquid crystalline behavior of columnar discotics and were characterized based on DSC analysis and polarized optical microscopy. The phase-transition temperatures and enthalpies of nickel complexes 1–3 are given in Table 1. Complexes with shorter carbon chain length,  $n=5-8$ , exhibited monotropic columnar phase behavior. On heating the crystals melt directly to isotropic liquids above 203.0–218.0 °C, whereas the transition of mesophases at *ca.* 187.0–219.0 °C took place on cooling from the isotropic phase. The temperature range of the mesophases was quite wide depending on the carbon chain length during the cooling process. The columnar rectangular phases<sup>4,8a</sup> were easily identified by observation of the mosaic textures displaying prominent wedge-shaped defect patterns (Fig. 1) under the polarized microscope. All these complexes were also studied at various temperatures by XRD to examine their mesophase structures. Rectangular<sup>4,8</sup> columnar phases often displayed two intense peaks in the low angle region, which were indexed as (200) and (110) reflections. The XRD data for the nickel complexes 1 and 2 are summarized in Table 2. For example, complexes  $n=5$  gave a diffraction of two strong reflections at  $d$  25.94 and 21.70 Å, a weaker peak at  $d$  8.57 Å and also a broad diffuse peak at  $d$  4.75 Å at 130 °C. This diffraction pattern (Fig. 2) corresponded to rectangular lattice constants:  $a=51.88$ ,  $b=23.89$  Å. Three different columnar Col<sub>rd</sub> phases<sup>4</sup> have now been identified:  $P(2_1/a)$ ,  $P(2/a)$  and  $C(2/m)$  depending on the point symmetry of the molecules. In rectangular phases the average molecular plane is not perpendicular to the column axis, and the tilt angle can be determined only by known molecular symmetry.

Interestingly, the nickel complexes with longer side chains,

**Table 1** Phase behavior<sup>a</sup> of nickel(II) complexes 1–3

1	<i>n</i> = 5	K <sub>1</sub>	79.9 (6.59)	K <sub>2</sub>	216.6 (5.46)	I
			35.7 (22.8)		Col <sub>rd</sub>	
6	6	K <sub>1</sub>	74.8 (37.7)	K <sub>2</sub>	224.5 (7.39)	I
			42.4 (36.7)		Col <sub>rd</sub>	
7	7	K <sub>1</sub>	27.2 (2.77)	K <sub>2</sub>	217.8 (4.87)	I
			42.2 (2.77)		Col <sub>rd</sub>	
8	8	K <sub>1</sub>	63.5 (28.7)	K <sub>2</sub>	217.8 (4.99)	I
			17.2 (29.8)		Col <sub>rd</sub>	
10	10	K <sub>1</sub>	73.6 (28.2)	K <sub>2</sub>	203.5 (4.91)	I
			21.1 (32.9)		Col <sub>hd</sub>	
12	12	K <sub>1</sub>	68.8 (12.0)	K <sub>2</sub>	189.9 (4.58)	I
			25.2 (46.6)		Col <sub>hd</sub>	
14	14	K <sub>1</sub>	72.4 (29.8)	K <sub>2</sub>	173.9 (2.31)	I
			44.8 (41.6)		Col <sub>hd</sub>	
2	14	K <sub>1</sub>	75.7 (24.2)	K <sub>2</sub>	158.0 (0.13)	I
			39.6 (24.7)		Col <sub>hd</sub>	
3	14	K <sub>1</sub>	76.1 (5.71)	K <sub>2</sub>	116.3 (52.1)	I
			56.9 (3.91)		Col <sub>hd</sub>	

<sup>a</sup>*n* represents the number of carbon atoms in the alkoxy chain. K<sub>1</sub>, K<sub>2</sub> = crystal phases; Col<sub>hd</sub> = columnar hexagonal disordered phase; Col<sub>rd</sub> = columnar rectangular disordered phase; I = isotropic. The transition temperatures (°C) and enthalpies (in parentheses, kJ mol<sup>-1</sup>) were determined by DSC at a scan rate of 10.0 °C min<sup>-1</sup>.



**Fig. 1** Optical texture (100×) observed for complex 1 (*n* = 8): Col<sub>rd</sub> phase at (a) 207 °C (thick sample) and (b) 195 °C (thin sample)

*n* = 10, 12 and 14, showed a typical columnar hexagonal phase. Two transitions<sup>10</sup> of crystal-to-columnar-to-isotropic (K→Col→I), and additional crystal-to-crystal (K<sub>1</sub>→K<sub>2</sub>) transitions were also observed for these complexes. From DSC analysis a typical larger enthalpy for the crystal-to-liquid crystal transition at lower temperatures (*ca.* 78.0 °C) and a lower enthalpy for the liquid crystal-to-isotropic transition at higher temperatures (174.0–190.0 °C) were observed. This lower value of the transition enthalpy indicated that the mesophases were relatively highly disordered. The temperature range of columnar mesophases for nickel complexes is quite wide (between 125–162 °C) in the cooling process and slightly sensitive to the carbon number of the side chains. The melting and clearing points both decrease as the side chain length increases. Upon heating, orange complexes melt to give birefringent fluid phases with columnar superstructures. When cooled from their isotropic phases, they displayed an optical texture (Fig. 3) which was a mixture of pseudo focal-conics and mosaic regions with linear birefringent defects, suggesting hexagonal columnar<sup>4,6,8</sup> structures. The existence of a large area of homeotropic domains may lead to the conclusion of preferred uniaxial character<sup>4a</sup> in this phase.

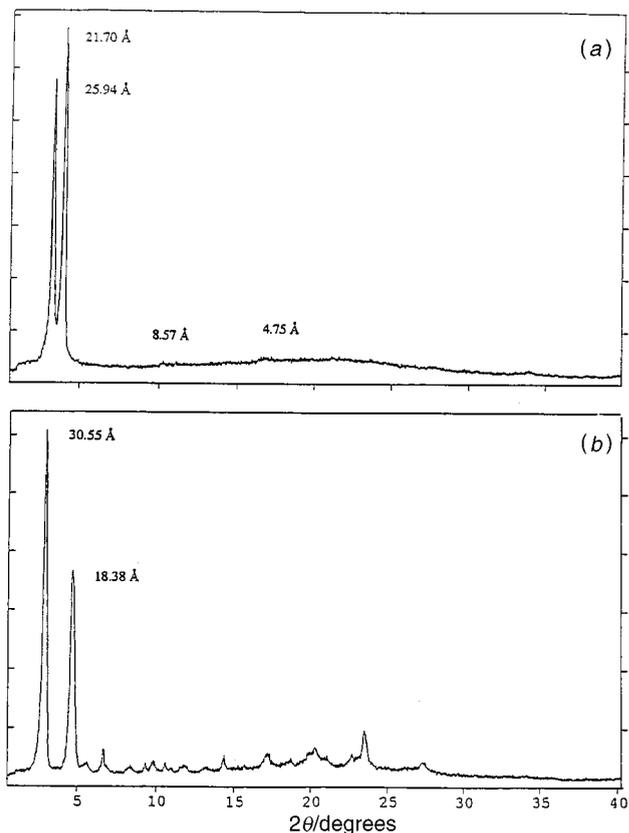
A summary of the diffraction peaks and lattice constants for these nickel complexes is also given in Table 1. For example, nickel complex 1 (*n* = 14) displays a diffraction pattern of a two-dimensional hexagonal lattice (Fig. 4) with an intense peak and two weaker peaks of 36.65, 21.77 and 18.86 Å at 155 °C. These are characteristic of the columnar hexagonal columnar (Col<sub>hd</sub>) phase with a *d*-spacing ratio of 1, (1/3)<sup>1/2</sup> and (1/4)<sup>1/2</sup>, corresponding to Miller indices (100), (110) and (200), respectively. This reflection pattern corresponds to an intercolumnar distance (a parameter of the hexagonal lattice) of 43.20 Å. In the hexagonal lattice the column axes are located along the *c* axis. However, a broad diffuse band, which is likely due to molten alkyl chains, occurred at 4.73–4.82 Å in the

**Table 2** Variable-temperature X-ray diffraction data for nickel(II) complexes **1** and **2**

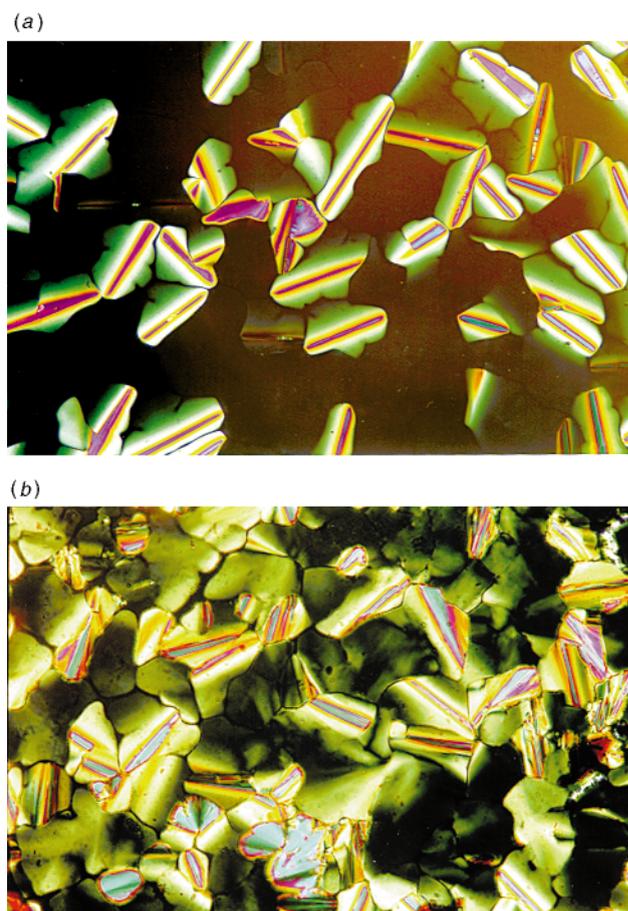
complex	<i>n</i>	mesophase	lattice spacing/Å	<i>d</i> -spacing/Å obs. (calcd.)	Miller indices
<b>1</b>	<i>n</i> =5	Col <sub>rd</sub> at 100 °C	<i>a</i> =52.28	26.14 (26.14)	(200)
			<i>b</i> =24.10	21.89 (21.89)	(110)
				8.57 (8.86)	(420)
		Col <sub>rd</sub> at 130 °C	<i>a</i> =51.88	25.94 (25.94)	(200)
			<i>b</i> =23.89	21.70 (21.70)	(110)
				8.57 (8.79)	(420)
	6	Col <sub>rd</sub> at 200 °C	<i>a</i> =54.44	27.22 (27.22)	(200)
			<i>b</i> =24.92	22.66 (22.66)	(110)
				12.58 (12.46)	(020)
	7	Col <sub>rd</sub> at 150 °C	<i>a</i> =58.08	29.04 (29.04)	(200)
			<i>b</i> =28.62	25.67 (25.67)	(110)
				16.30 (16.03)	(310)
8	Col <sub>rd</sub> at 200 °C	<i>a</i> =56.84	28.42 (28.42)	(200)	
		<i>b</i> =28.23	25.28 (25.28)	(110)	
			5.18 (br)		
10	Col <sub>hd</sub> at 100 °C	<i>a</i> =37.49	32.40 (32.40)	(100)	
			18.60 (18.70)	(110)	
			16.38 (16.20)	(200)	
	Col <sub>hd</sub> at 190 °C	<i>a</i> =37.03	32.07 (32.07)	(100)	
			18.39 (18.51)	(110)	
			16.08 (16.03)	(200)	
12	Col <sub>hd</sub> at 120 °C	<i>a</i> =40.64	35.63 (35.63)	(100)	
			21.17 (20.57)	(110)	
			17.58 (17.81)	(200)	
14	Col <sub>hd</sub> at 155 °C		4.79 (br)		
			36.65 (36.65)	(100)	
			21.77 (21.60)	(110)	
			18.86 (18.32)	(200)	
			4.82 (br)		
			38.04 (38.04)	(100)	
<b>2</b>	14	Col <sub>hd</sub> at 120 °C	<i>a</i> =43.92	38.04 (38.04)	(100)
				21.85 (21.96)	(110)
				19.62 (19.62)	(200)
				4.78 (br)	

wide-angle region. The absence of distinct peaks at a high angle rules out the existence of periodicity along the columns, and is also consistent with the DSC analysis showing low enthalpies for the columnar-to-isotropic transition. This positively indicates a highly disordered mesophase; *i.e.* there is no long-range order along the columns. The temperature dependence of the lattice parameters in these complexes was also studied. We find that the low-angle reflections of complexes generally shift to a larger *d*-spacing with decreasing temperatures (*i.e.* *d*=37.03 Å at 190 °C and *d*=37.49 Å at 100 °C for complex **1**; *n*=10). The hexagonal lattices are also correlated well with increasing side chain length.

The mesophase change of columnar rectangular to hexagonal arrangements with increasing side chain length was observed in this system; with increasing carbon number the hexagonal phase arrangement predominates over the rectangular phase. The mesophase crossover from Col<sub>rd</sub> to Col<sub>hd</sub> has been observed in similar metallomesogenic systems, and was generally attributed to the greater core interaction necessary for the formation of the Col<sub>rd</sub> phases. The tilted Col<sub>rd</sub> phase reduced the interactions between the bulky side chains and allowed closer contacts between the cores. Similar mesophase crossover was also observed in systems<sup>4,8a,b,d</sup> with the larger Pd replacing Cu in the Cu analogue.<sup>8a</sup> This pseudohexagonal lattice constant, *i.e.* a rectangular lattice with an axial ratio of *b/a* from the ideal hexagonal of 3<sup>1/2</sup> (Scheme 3), for this series of nickel complexes was in the range of 2.01–2.18 (from



**Fig. 2** X-Ray diffraction data for complex **1** (*n*=5): (a) Col<sub>rd</sub> phase at 130 °C and (b) K phase at room temperature



**Fig. 3** Optical texture (100 ×) observed for complex **1** (*n*=12): (a) Col<sub>hd</sub> phase at 180 °C and (b) K phase at room temperature

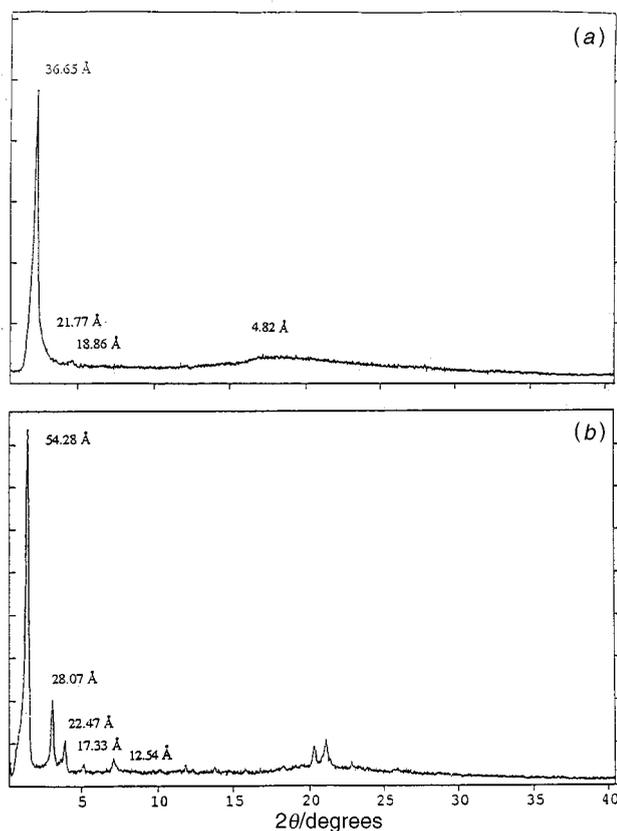
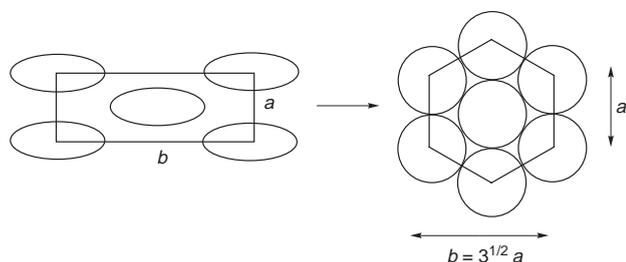


Fig. 4 X-Ray diffraction data for complex **1** ( $n=14$ ): (a)  $\text{Col}_{\text{hd}}$  phase at  $155^\circ\text{C}$  and (b) K phase at room temperature



Scheme 3

$n=5-10$ ). This value indicated that the structural departure from the ideal hexagonal lattice was about 20% in this system.

### Complexes 2 and 3 with eight and six side chains

Nickel complexes **2** and **3** ( $n=14$ ) were also prepared to study the effect of side chain density on the formation of mesophases. DSC analysis and XRD diffraction showed that complex **2** with eight side chains exhibited a similar columnar hexagonal disordered phase ( $\text{Col}_{\text{hd}}$ ). The isotropic point for the complex was *ca.*  $20^\circ\text{C}$  lower, and the temperature of the mesophase was narrower than for the similar complex **1** ( $n=14$ ). This result indicated that higher side chain density tended to easily stabilize the mesogenic core, as is often observed in this type of columnar system. However, complex **3** ( $n=14$ ) with six side chains showed only a transition of the crystal to isotropic phase at  $116.3^\circ\text{C}$ . Similar nickel complexes ( $n=12$ ) of disc-like molecules have also been prepared, in which nickel complexes<sup>10</sup> with two or four dodecyloxy chains were found to be non-mesogenic. The broadening<sup>10</sup> of the molecular width and the non-coplanarity of the benzylidene ring were attributed to this non-mesomorphic behavior.

## Conclusion

The mesomorphic studies of the title nickel complexes indicated that the formation of columnar phases was found to be strongly dependent on the number of side chains around the core group. The complexes with a total of ten and eight side chains exhibited columnar phases, however, complexes with six and four side chains exhibited crystalline phases. Therefore, the number of side chains for this type of disc-like nickel complexes studied must be at least eight to form a stable mesogen.

## Experimental section

All chemicals and solvents were reagent grade from Aldrich Chemical Co., and used without further purification.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were measured on a Bruker DRS-200.  $J$  Values are in Hz. Infrared spectra were recorded on a Bio-Rad FTS-155 using polystyrene as a standard. DSC thermographs were recorded on a Perkin-Elmer DSC-7 and calibrated with a pure indium sample. All phase behavior was determined at a scan rate of  $10.0^\circ\text{C min}^{-1}$  unless otherwise noted. Optical polarized microscopy was carried out on a Nikon MICROPHOT-FXA with a Mettler FP90/FP82HT hot stage system. X-Ray powder diffraction (XRD) studies were conducted on an INEL MPD-diffractometer with a 2 kW Cu-K $\alpha$  X-ray source equipped with an INEL CPS-120 position sensitive detector and a variable temperature capillary furnace with an accuracy of  $\pm 0.10^\circ\text{C}$  in the vicinity of the capillary tube. The detector was calibrated using mica and silicon standards. The powder samples were charged in Lindemann capillary tubes (80 mm long and 0.01 mm thick) from Charles Supper Co. with a diameter of 0.1 or 0.2 mm, and the end was flame sealed. The samples were heated above the isotropic temperatures and left for *ca.* 10 min. The samples were then cooled at a rate of  $5.0^\circ\text{C min}^{-1}$  to the desired temperature and the diffraction data collected. The methyl 3,4,5-trialkoxybenzoate esters, methyl 4-alkoxybenzoate esters, ethyl 3,4-dialkoxybenzoate esters, and 3,4-dialkoxybenzaldehyde were prepared by literature<sup>2a-d,6a</sup> procedures.

### Methyl 4-tetradecyloxybenzoate

White solid, yield 90%.  $\delta_{\text{H}}(\text{CDCl}_3)$ : 0.82 (t,  $J$  6.73,  $-\text{CH}_3$ , 3H), 1.24–1.84 [m,  $-(\text{CH}_2)_{12}$ , 24H], 3.85 (s,  $-\text{OCH}_3$ , 3H), 4.27 (t,  $J$  7.31,  $-\text{OCH}_2$ , 2H), 6.84 (d,  $J$  8.82,  $-\text{C}_6\text{H}_4$ , 2H), 7.92 (d,  $J$  8.82,  $-\text{C}_6\text{H}_4$ , 2H).  $\delta_{\text{C}}(\text{CDCl}_3)$ : 14.76, 23.26, 26.58, 29.79, 29.98, 30.05, 30.30, 30.33, 30.36, 32.53, 52.54, 68.83, 114.62 ( $\text{C}^{2,6}$ ), 122.91 ( $\text{C}^1$ ), 132.13 ( $\text{C}^{3,5}$ ), 163.45 ( $\text{C}^4$ ), 167.53 ( $\text{C}=\text{O}$ ).

### Ethyl 3,4-bis(tetradecyloxy)benzoate

White solid, yield 89%.  $\delta_{\text{H}}(\text{CDCl}_3)$ : 0.87 (t,  $-\text{CH}_3$ , 9H), 1.24–1.83 (m,  $-\text{CH}_2$ , 44H), 3.97 (t,  $J$  8.19,  $\text{OCH}_2$ , 2H), 4.34 (tt,  $-\text{OCH}_2$ , 2H), 6.80 (d,  $J$  8.44,  $-\text{C}_6\text{H}_3$ , 1H), 7.51 (s,  $-\text{C}_6\text{H}_3$ , 1H), 7.57 (d,  $J$  6.42,  $-\text{C}_6\text{H}_3$ , 1H).  $\delta_{\text{C}}(\text{CDCl}_3)$ : 13.91, 14.21, 22.51, 25.84, 28.93, 29.21, 31.74, 60.48, 68.84, 69.13, 111.7 ( $\text{C}^6$ ), 114.2 ( $\text{C}^2$ ), 122.6 ( $\text{C}^5$ ), 123.2 ( $\text{C}^1$ ), 148.3 ( $\text{C}^4$ ), 152.9 ( $\text{C}^3$ ), 166.3 ( $\text{C}=\text{O}$ ).

### Methyl 3,4,5-tris(dodecyloxy)benzoate

White solid, yield 90%.  $\delta_{\text{H}}(\text{CDCl}_3)$ : 0.86 (t,  $-\text{CH}_3$ , 9H), 1.26–1.84 (m,  $\text{CH}_2$ , 60H), 3.88 (s,  $-\text{OCH}_3$ , 3H), 4.03 (tt,  $-\text{OCH}_2$ , 6H), 7.25 (s,  $\text{C}_6\text{H}_2$ , 2H).  $\delta_{\text{C}}(\text{CDCl}_3)$ : 14.18, 22.75, 26.14, 29.36, 29.45, 29.62, 29.71, 29.75, 29.39, 30.39, 32.00, 52.13, 69.22, 75.53, 105.02 ( $\text{C}^{2,6}$ ), 124.69 ( $\text{C}^1$ ), 142.01 ( $\text{C}^{3,5}$ ), 152.83 ( $\text{C}^4$ ), 166.89 ( $\text{C}=\text{O}$ ).

### 3,4-Bis(dodecyloxy)benzaldehyde

White crystals, yield 85%.  $\delta_{\text{H}}(\text{CDCl}_3)$ : 0.85 (t,  $J$  6.79,  $\text{CH}_3$ , 6H), 1.23–1.43 (m,  $\text{CH}_2$ , 36H), 1.74–1.86 (m,  $\text{CH}_2$ , 4H), 4.03 (tt,  $-\text{OCH}_2$ , 4H), 6.96 (d,  $J$  8.63,  $\text{C}_6\text{H}_3$ , 1H), 7.36 (s,  $\text{C}_6\text{H}_3$ , 1H), 7.48 (d,  $J$  1.81,  $\text{C}_6\text{H}_3$ , 1H), 9.79 (s, CHO, 1H).  $\delta_{\text{C}}(\text{CDCl}_3)$ : 14.03, 22.63, 25.94, 28.98, 29.06, 29.31, 29.57, 31.88, 69.10, 111.1 ( $\text{C}^6$ ), 111.8 ( $\text{C}_2$ ), 126.4 ( $\text{C}_5$ ), 129.9 ( $\text{C}_1$ ), 149.5 ( $\text{C}^4$ ), 154.7 ( $\text{C}^3$ ), 190.8 ( $\text{C}=\text{O}$ ).

### 4-Tetradecyloxybenzoylhydrazine

White solid, yield 90%.  $\delta_{\text{H}}(\text{CDCl}_3)$ : 0.84 (t,  $J$  6.30,  $-\text{CH}_3$ , 3H), 1.23–1.83 (m,  $-\text{CH}_2$ , 24H), 3.28 (br,  $-\text{OCNHNH}_2$ , 2H), 3.92 (t,  $J$  6.47,  $-\text{OCH}_2$ , 2H), 6.79 (d,  $J$  8.76,  $-\text{C}_6\text{H}_4$ , 2H), 7.73 (d,  $-\text{C}_6\text{H}_4$ , 2H), 8.53 (br,  $-\text{CONH}$ , 1H).  $\delta_{\text{C}}(\text{CDCl}_3)$ : 13.94, 16.26, 22.51, 25.37, 25.81, 28.94, 29.18, 29.46, 30.74, 31.74, 68.05, 114.14 ( $\text{C}^{2,6}$ ), 125.24 ( $\text{C}^1$ ), 129.04 ( $\text{C}^{3,5}$ ), 161.89 ( $\text{C}^4$ ), 168.74 ( $\text{C}=\text{O}$ ).

### 3,4-Bis(tetradecyloxy)benzoylhydrazine

White solid, 78%.  $\delta_{\text{H}}(\text{CDCl}_3)$ : 0.85 (t,  $J$  6.69,  $-\text{CH}_3$ , 6H), 1.23–1.84 (m,  $-\text{CH}_2$ , 48H), 3.72 (br,  $-\text{OCNHNH}_2$ , 2H), 4.05 (tt,  $-\text{OCH}_2$ , 4H), 6.83 (d,  $J$  8.47,  $-\text{C}_6\text{H}_3$ , 1H), 7.51 (s,  $-\text{C}_6\text{H}_3$ , 1H), 7.58 (br,  $-\text{CONH}$ , 1H), 7.62 (d,  $J$  8.39,  $-\text{C}_6\text{H}_3$ , 1H).  $\delta_{\text{C}}(\text{CDCl}_3)$ : 13.93, 14.22, 22.53, 25.84, 28.92, 29.04, 29.22, 31.77, 68.81, 69.10, 111.71 ( $\text{C}^3$ ), 114.13 ( $\text{C}^4$ ), 122.58 ( $\text{C}^1$ ), 123.28 ( $\text{C}^5$ ), 148.31 ( $\text{C}^2$ ), 152.95 ( $\text{C}^6$ ), 168.12 ( $\text{C}=\text{O}$ ).

### 3,4,5-Tris(dodecyloxy)benzoylhydrazine

White solid, yield 80%.  $\delta_{\text{H}}(\text{CDCl}_3)$ : 0.82 (t,  $J$  7.46,  $-\text{CH}_3$ , 3H), 1.23–1.81 (m,  $-\text{CH}_2$ , 60H), 3.33 (br,  $-\text{CONHNH}_2$ , 2H), 3.96 (tt,  $J$  6.16,  $-\text{OCH}_2$ , 6H), 6.90 (s,  $-\text{C}_6\text{H}_2$ , 2H), 7.34 (br,  $-\text{CONH}$ , 1H).  $\delta_{\text{C}}(\text{CDCl}_3)$ : 14.09, 22.67, 26.05, 29.29, 29.34, 29.37, 29.55, 30.28, 31.90, 69.27, 73.50, 105.41, 127.38 ( $\text{C}^{2,6}$ ), 141.33 ( $\text{C}^1$ ), 153.16 ( $\text{C}^{3,5}$ ), 168.62 ( $\text{C}=\text{O}$ ).

### *N*-(3,4-Dialkoxybenzylidene)-*N'*-(3',4',5'-trialkoxybenzoyl)hydrazine

$\nu/\text{cm}^{-1}$  (thin film): 3421, 2923, 2847, 1640, 1626, 1599, 1576, 1514, 1470, 1437, 1387, 1337, 1264, 1233, 1177, 1144, 1069, 1069.

#### General procedures for preparation of nickel complexes.

#### Bis[*N*-(3,4-diheptyloxybenzylidene)-*N'*-(3',4',5'-triheptyloxybenzoyl)hydrazinato]nickel(II)

A suspension of *N*-(3,4-diheptyloxybenzylidene)-*N'*-(3',4',5'-triheptyloxybenzoyl)hydrazine (0.31 g, 0.342 mmol) and nickel acetate (0.090 g, 0.362 mmol) in 100 ml of absolute ethanol was heated under reflux overnight. The orange solid was filtered off, and then washed with hot ethanol ( $3 \times 20$  ml). The product was isolated as orange crystals after twice recrystallization from THF–ethanol. Yield 73%.  $\nu/\text{cm}^{-1}$  (thin film): 2929, 2855, 1597, 1522, 1502, 1466, 1473, 1397, 1362, 1273, 1221, 1180, 1137, 1069, 1038. (Calc. for  $\text{C}_{138}\text{H}_{242}\text{N}_4\text{O}_{12}\text{Ni}$ : C 71.46, H 9.91, N 3.40. Found C 71.17, H 10.06, N 3.44%).

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