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Discotic Liquid Crystals of Transition Metal Complexes 14[1]: The Columnar Mesomorphism of the Branched-chain-substituted Tetrakis(dithioacetato)-dinickel(II) Complex

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The *n*-alkyl derivative of tetrakis(*n*-pentyldithiolato)dinickel(II), **1a**, has a monotropic discotic lamellar (D_L) phase, whereas the branched-chain-substituted derivative of tetrakis(1-ethylpentyldithiolato)dinickel(II), **1b**, has both an enantiotropic discotic hexagonal disordered columnar (D_{hd}) mesophase and a monotropic D_L mesophase. Thus, we could change the mesomorphism from lamellar to columnar by changing the *n*-alkyl chain to the branched chain. This is a new branching effect, because this phenomenon has not been reported to date in the literature.

INTRODUCTION

Some effects of the introduction of branched-chains into mesogens on the mesomorphism have been reported.[2–17] As far as we know, they can be summarized as five effects:

(1) their melting points and clearing points are lowered:
  (i) their clearing points are lowered,[2–5]
  (ii) although their mesogenic properties remain, the melting points from the crystal to the mesophase are lowered; e.g., discotic mesomorphic temperature ranges expand.[6–8]
(2) a certain mesomorphic range expands or narrows:
  (iii) the mesomorphic range of the smectic C phase is expanded,[3]
  (iv) the mesomorphic range of the smectic A phase expands[9] or narrows,[3,5]
(3) the kinds of mesophase change:
  (v) methylation at the 1-position of the *n*-alkyl group gives no mesogen while methylation at the terminal position gives more mesomorphic polymorphs[10];

such effect appears also in discotic liquid crystals,[6]
(vi) ethylation at the 2-position of the side chains in octa-substituted phthalocyanine gives a tetragonal columnar mesophase[12] and a discotic nematic phase, whereas the straight alkyl-chain-substituted phthalocyanines give hexagonal columnar mesophases,[11]

(4) a nematic (N) phase or a cholesteric (Ch) phase appears:
(vii) a nematic phase is added,[13]
(viii) a S_B and/or a S_c mesophase disappears while a N mesophase appears,[14]
(ix) chiral-branched chains give a discotic cholesteric mesophase,[15]

(5) all mesophases disappear or a mesophase appears:
(x) only di*iso*butyl silanediol shows discotic columnar mesomorphism while *n*-alkyl chain-substituted derivatives do not show any mesomorphism,[16,17]
(xi) substitution at the 1- and 3-position with the methyl groups bears the monotropic nematic mesophase or the disappearance of the nematic one.[2,4,5,9]

In our previous paper,[18] we found that the straight-chain-substituted complexes, tetrakis(*n*-alkyldithiolato)dinickel(II), show a **monotropic** discotic *lamellar* (D_L) phase. In this report, we wish to report that a branched-chain-substituted complex, tetrakis(1-ethylpentyldithiolato)dinickel(II), shows an **enantiotropic** discotic hexagonal *columnar* phase (Figure 1). This branching effect is different from the effects (i)–(xi) mentioned above.

EXPERIMENTAL

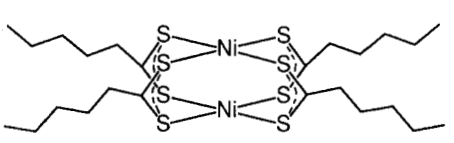
Synthesis

The synthetic route for tetrakis(*n*-pentyldithiolato)dinickel(II), **1a**, and tetrakis(1-ethylpentyldithiolato)dinickel(II), **1b**, is shown in Scheme I. The detailed procedure has been previously reported.[18] Since the purification of **1b** was different from the conventional one of **1a**,[18] the purification of **1b** is reported here.

The reaction mixture was filtered and a black viscous residue was washed with CCl_4 to remove yellow species. The target complex was in the filtrate. The filtrate was evaporated and recrystallized from *n*-hexane to afford red-violet needle-like crystals. Yield 36.6%. Anal. Calcd. for $C_{32}H_{60}S_8Ni_2$: C, 46.94; H, 7.39. Found: C, 46.98; H, 7.38.

Measurements

The phase transition behavior of the complex was observed by a polarizing microscope equipped with a heating plate controlled by a thermoregulator, Mettler FP80 and FP82, and measured with a differential scanning calorimeter, Rigaku Thermaflex TG-DSC. To establish the mesophases, X-ray diffraction powder measurements were performed with Cu-Kα radiation using a Rigaku Geigerflex equipped with a hand-made heating plate controlled by a thermoregulator.[19] UV-VIS spectra of the complex in chloroform were recorded by a Hitachi 330 spectrophotometer.

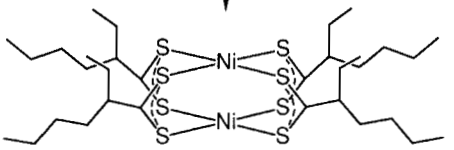


Monotropic

Lamellar

Mesophase (D_L)

1a



Enantiotropic

Hexagonal Columnar

Mesophase (D_{hd})

+

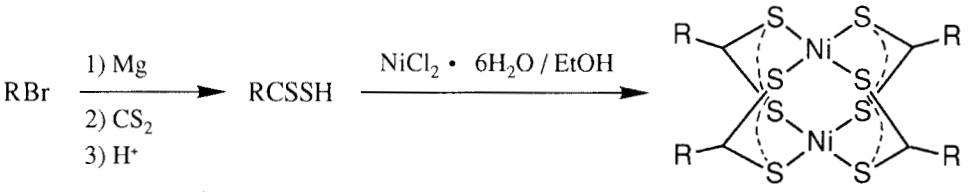
1b

Monotropic

Lamellar

Mesophase(D_L)

FIGURE 1 Formulae of the complexes **1a** and **1b**.



1

a : R=$CH_2(CH_2)_3CH_3$

b : R=$\underset{\displaystyle CH_2CH_3}{\overset{\displaystyle CH_2(CH_2)_3CH_3}{|}}$

SCHEME I Synthetic route for tetrakis(alkyldithiolato)dinickel(II) complexes, **1**.

RESULTS AND DISCUSSION

In Table I are summarized the phase transition temperatures and enthalpy changes of **1a** and **1b**, measured by the DSC and the polarizing microscope. It was reported

TABLE I

Phase transition temperatures(T) and enthalpy changes(ΔH) of **1a** and **1b**

Complex	Phase[a] $\xrightarrow[\Delta H(kJ/mol)]{T(^\circ C)}$ Phase
	⇝ relaxation
1a	$K \xrightarrow[46.9]{79.0} I.L.$; $I.L. \rightarrow D_L$ (43.1) ; $D_L \rightsquigarrow K$
1b	$K_1 \xrightarrow[2.0]{64} K_2 \xrightarrow[20.6]{124} D_{hd} \underset{39.8}{\overset{151}{\rightleftharpoons}} I.L.(*)$; $I.L.(*) \rightarrow D_L$; $D_L \xrightarrow{ca.100} K_3$

[a] Phase nomenclature: K = crystal, D_L = discotic lamellar mesophase, D_{hd} = discotic hexagonal disorderd columnar mesophase, and I.L. = isotropic liquid.

* Gradual decomposition: see the main text.

in the previous paper[18] that complex **1a** has a monotropic discotic lamellar (D_L) mesophase. On the other hand, it was found here that complex **1b** has both an enantiotropic discotic hexagonal disordered columnar (D_{hd}) mesophase and a monotropic D_L mesophase.

When the sample of complex **1b** was pressed at ca. 130°C under the polarizing microscope, it showed high viscosity with birefringence, which is one of the characteristics of liquid crystalline phases. On further heating, it cleared into an isotropic liquid (I.L.) at 151°C. On further heating over this temperature, the red sample became brown, which indicated that it began to decompose. In Figure 2 are illustrated the DSC thermogram and the thermogravimetric analysis (TG) thermogram of the virgin sample of **1b** on the first heating run at a heating rate of 10°C/min. The TG thermogram shows a weight loss around 160°C immediately after the clearing point. In order to prevent its decomposition as much as we can, the sample after clearing was cooled immediately to r.t. This rapidly cooled sample (non-virgin sample) showed a different liquid crystalline phase inthe second heating run. To distinguish these different mesophases, we carried out X-ray diffraction measurements.

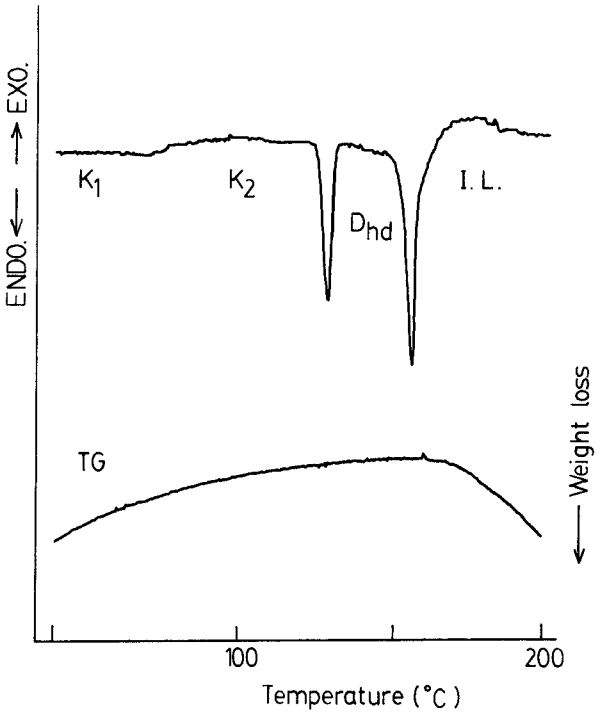


FIGURE 2 DSC and TG thermograms of the complex **1b**. Heating rate: 10°C/min.

Figure 3 shows the X-ray diffraction powder pattern of the virgin sample of **1b** at 135°C. It gave four narrow reflections at d = 12.9, 7.49, 6.49, and 4.88 Å. They could be assigned (100) (110) (200) and (210) planes in a two-dimensional hexagonal lattice, respectively. So it could be concluded that this mesophase is a discotic hexagonal disordered columnar (D_{hd}) phase. Figure 4 shows the X-ray diffraction powder pattern of the non-virgin sample of **1b** at 111°C. This non-virgin sample was made by heating the virgin sample up to 155°C and then cooling immediately to r.t. This diffraction pattern gave three narrow peaks at d = 13.4, 6.73, and 4.47 Å. These spacings are in a ratio 1: 1/2: 1/3, which is characteristic of lamellar structures. In addition to these, two small peaks were observed at d = 12.9 and 11.5 Å, which may be attributable to the reflections of the remaining D_{hd} mesophase or the impurities from decomposition. Nevertheless, it could be concluded from this pattern that the mesophase is a lamellar liquid crystal. In Table II are summarized these X-ray diffraction data.

As illustrated in Scheme II, it has been reported that the tetrakis-form transforms into the bis-form by heating or in a chloroform solution for a long time.[18] From this fact, one question may arise: since it is possible that a disk-like tetrakis-form transforms into a rod-like bis-form, is this phase not a discotic lamellar mesophase but a rod-like smectic mesophase? Figure 5 shows UV-VIS absorption spectra of **1b** in chloroform. Immediately after the crystals of **1b** were dissolved in chloroform, the absorbance at 273 nm due to the tetrakis-form (red) became smaller with time, while the absorbance at 321 nm due to the bis-form (yellow) became bigger. In

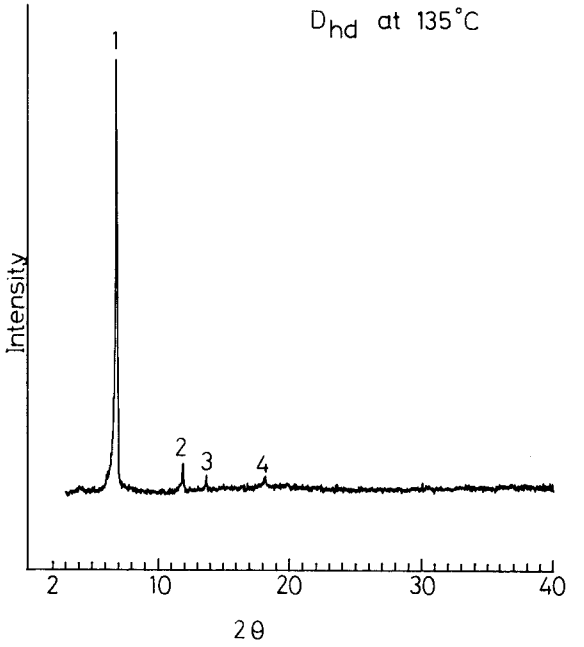


FIGURE 3 X-Ray diffraction powder pattern of the complex **1b** (virgin sample) at 135°C.

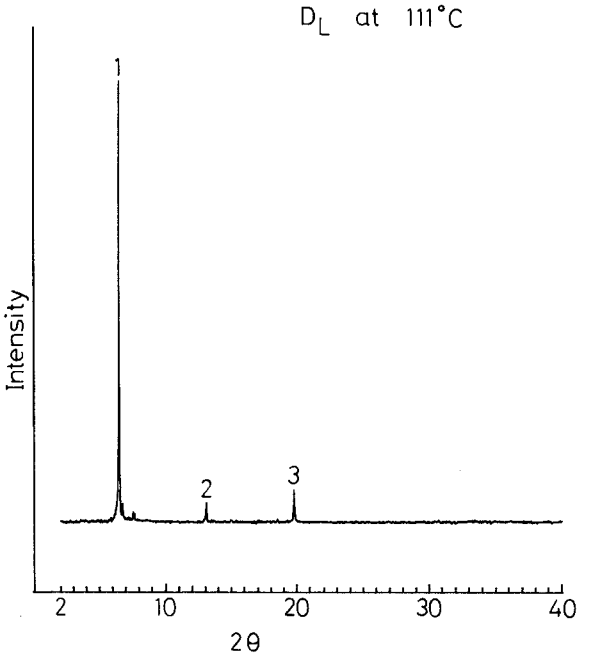


FIGURE 4 X-Ray diffraction powder pattern of the complex **1b** (non-virgin sample) at 111°C.

TABLE II

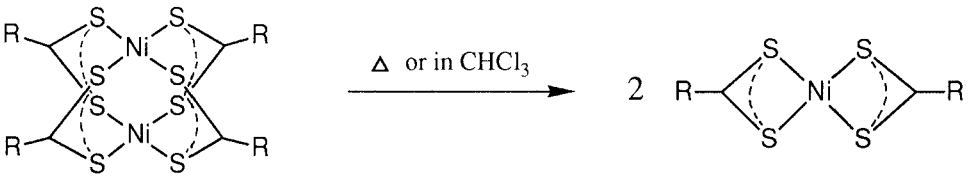
X-ray diffraction data for the D_{hd} mesophase in the virgin sample of **1b** at 135°C and the D_L mesophase in the non-virgin sample of **1b** at 111°C

1) T = 135°C; D_{hd} in the virgin sample of **1b**: a = 15.0 Å

Peak No.	Measured lattice spacing(Å)	Calculated lattice spacing(Å)	Miller indices (hkl)
1	12.9	13.0	(100)
2	7.49	7.47	(110)
3	6.49	6.48	(200)
4	4.88	4.89	(210)

2) T = 111°C; D_L in the non-virgin sample of **1b**: c = 13.4 Å

Peak No.	Measured lattice spacing(Å)	Calculated lattice spacing(Å)	Miller indices (hkl)
1	13.4	13.4	(001)
2	6.73	6.70	(002)
3	4.47	4.47	(003)



Tetrakis-form Bis-form

SCHEME II Irreversible transformation from the tetrakis-form to the bis-form.

Figure 6, the ratios of the absorbances at 273 nm and 321 nm, ($A_{273-278}/A_{321-328}$), are plotted against the passage of time after the crystals of **1b** were dissolved in chloroform. When the value of the ratio is small, the tetrakis-form exists predominantly, and when it becomes bigger, the bis-form is produced more. Hereupon, the non-virgin sample which had been used for the X-ray analysis in Figure 4 was dissolved in chlorofom and then immediately its UV-VIS spectrum was measured.

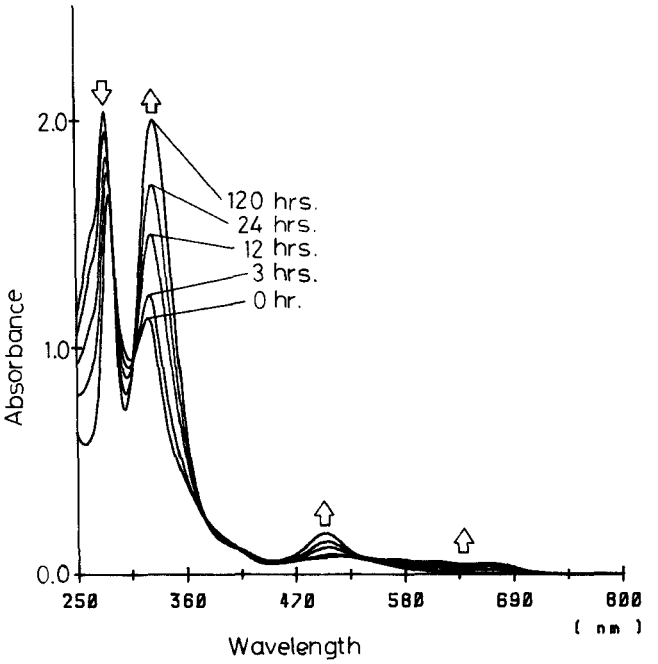


FIGURE 5 Electronic spectral changes of the complex **1b** in chloroform at time intervals after the preparation of the solution.

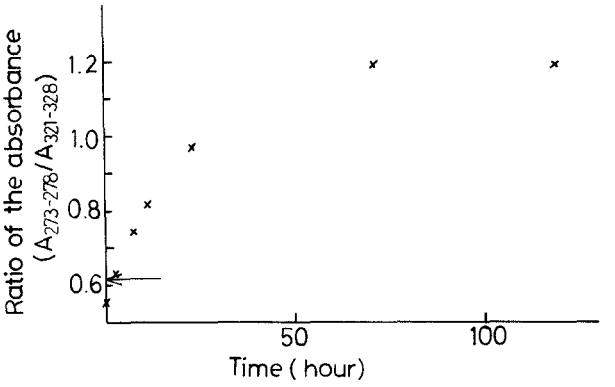


FIGURE 6 Ratio of the absorbances ($A_{273-278}/A_{321-328}$) in chloroform solution changes at time intervals after the preparation of the solution.

The ratio was 0.61 as shown in Figure 5 with an arrow. From this value, it could be tentatively deduced that this lamellar phase is a discotic lamellar (D_L) mesophase[20] because the non-virgin sample kept the disk-like molecular structure of the tetrakisform. Therefore, both a discotic hexagonal columnar (D_{hd}) phase and a discotic lamellar (D_L) phase appear in the same compound, which is the first example of its kind in liquid crystals.

CONCLUSION

The *n*-alkyl derivative of tetrakis(*n*-pentyldithiolato)dinickel(II), **1a**, has a monotropic D_L phase, whereas the branched-chain-substituted derivative of tetrakis(1-ethyl-pentyldithiolato)dinickel(II), **1b**, has both an enantiotropic D_{hd} mesophase and a monotropic D_L mesophase. Thus, we could change the mesomorphism from lamellar to columnar by changing the *n*-alkyl chain to the branched chain. This is a new branching effect, because this phenomenon has not been reported to date in the literature.

References

1. Part 13: K. Ohta, H. Hasebe, M. Moriya, T. Fujimoto and I. Yamamoto, *Mol. Cryst. Liq. Cryst.*, in press.
2. G. W. Gray and J. Harrison, *Mol. Cryst. Liq. Cryst.*, **13**, 37 (1971).
3. M. E. Neubert, K. Leung, S. J. Laskos, Jr., M. C. Ezenyilimba, M. R. Jirousek, D. Leonhardt, B. A. Williams and B. Ziemnicka-Merchant, *Mol. Cryst. Liq. Cryst.*, **166**, 181 (1989).
4. M. E. Neubert and D. Leonhardt, *Mol. Cryst. Liq. Cryst.*, **172**, 227 (1989).
5. Y. Matsunaga and N. Miyajima, *Mol. Cryst. Liq. Cryst.*, **178**, 157 (1990).
6. S. Tsuchiya, *Inorg. Chem.*, **24**, 4452 (1985).
7. D. M. Collard and C. P. Lillya, *J. Am. Chem. Soc.*, **111**, 1829 (1989).
8. G. S. Attard and P. R. Cullum, *Liq. Cryst.*, **8**, 299 (1990).
9. Y. Matsunaga, H. Matsuzaki and N. Miyajima, *Bull. Chem. Soc. Jpn.*, **63** 886 (1990).
10. Y. Matsunaga and H. Matsuzaki, *Bull. Chem. Soc. Jpn.*, **62**, 3417 (1989).
11. D. Leliévre, M. A. Petit and J. Simon, *Liq. Cryst.*, **4**, 707 (1989).
12. K. Ohta, T. Watanabe, H. Hasebe, Y. Morizumi, T. Fujimoto, I. Yamamoto, D. Leliévre and J. Simon, *Mol. Cryst. Liq. Cryst.*, **196**, 13 (1991).
13. Y. Matsunga and N. Miyajima, *Bull. Chem. Soc. Jpn.*, **57**, 1413 (1984).
14. Y. Matsunaga and N. Miyajima, *Mol. Cryst. Liq. Cryst.*, **116**, 207 (1985).
15. I. Cho and Y. Lim, *Mol. Cryst. Liq. Cryst.*, **154**, 9 (1988); I. Cho and Y. Lim, *Chem. Lett.*, 2107 (1987).
16. C. Eaborn and N. H. Hartshorne, *J. Chem. Soc.*, **549**, (1955).
17. J. D. Bunning, J. E. Lydon, C. Eaborn, P. M. Jackson, J. W. Goodby and G. W. Gray, *J. Chem. Soc., Faraday Trans. I*, **78**, 713 (1982).
18. K. Ohta, H. Ema, I. Yamamoto and K. Matsuzaki, *Liq. Cryst.*, **3**, 1671 (1988).
19. H. Ema, Master thesis, Shinshu University, Ueda, Chap. 7, 1988.
20. K. Ohta, H. Muroki, A. Takagi, K. Hatada, H. Ema, I. Yamamoto and K. Matsuzaki, *Mol. Cryst. Liq. Cryst.*, **140**, 131 (1986); H. Sakashita, A. Nishitani, Y. Sumiya, H. Terauchi, K. Ohta and I. Yamamoto, *ibid.*, **163**, 211 (1988).