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Discotic Liquid Crystals of Transition Metal Complexes VI. Monotropic Lamella Mesomorphism of Tetrakis(*N*-Alkyldithiolato)Dinickel(II) and Bis(*N*-Alkylxanthato)Nickel(II) Complexes

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Discotic liquid crystals of transition metal complexes†

VI. Monotropic lamella mesomorphism of tetrakis(*n*-alkyldithiolato)dinickel(II) and bis(*n*-alkylxanthato)nickel(II) complexes

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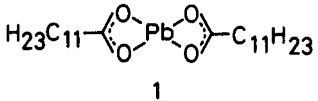
It was found that each of the tetrakis(*n*-alkyldithiolato)dinickel(II), $(C_n\text{-DTA})_4\text{-}Ni_2$, complexes where *n*-alkyl is *n*-pentyl through *n*-dodecyl, exhibits a broken-fan texture on cooling from an isotropic liquid, and that the phase gave a characteristic lamella structure X-ray diffraction powder pattern. Furthermore, the infrared spectrum of this phase is more similar to that of the isotropic liquid than that of the crystal. Therefore, the phase can be described as a monotropic lamella mesophase. Interestingly, each of the complexes of bis(*n*-alkylxanthato)nickel(II), $(C_n\text{-Xan})_2Ni$, ($n = 5, 7, 9, 11$) exhibits double (triple) melting behavior via the isotropic liquid, whereas each of the complexes of $(C_n\text{-Xan})_2Ni$ ($n = 4, 6, 8, 10, 12$) shows ordinary single melting behavior. Such unique double melting accompanied by an even–odd effect appears to be the first example of this in the long chain substituted compounds. Each of the complexes of $(C_n\text{-Xan})_2Ni$ ($n = 9, 11, 12$) has a monotropic lamella mesophase exhibiting a large broken fan texture.

1. Introduction

To date, there have been very few reports of liquid crystals of organic transition metal complexes. However, they may have the following merits if synthesized: (1) potential application in colour displays, magnetic devices [2], electric conductors



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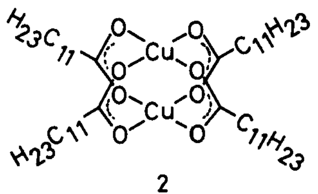

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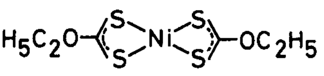

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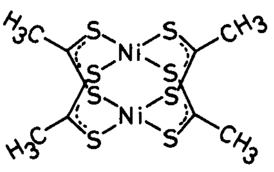

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†For Part V see [1].

[3], catalysts, and so on; (2) one can synthesize freely a great variety of the organic ligands by ordinary organic synthetic methods, although it is very difficult for the inorganic ligands; (3) even for the same ligand, one can easily change the molecular structure by changing the central transition metal [4, 5]. For example, lead(II) dodecanoato (formula 1) has two different *classic* mesomorphism between 85°C and 114°C. The higher temperature (96°C–114°C) mesophase was assigned as a smectic A [4]. On the other hand, copper(II) dodecanoato (formula 2) has the same ligand as the lead(II) dodecanoato but a different molecular structure. This dicopper complex exhibits a *discotic* columnar mesophase (D_h) at temperatures above 107°C [5].

Thus, one can change the molecular and mesomorphic structures by changing the central transition metal even for the same ligands. This sort of change could not be easily achieved for pure organic compounds instead of organic transition metal complexes. Furthermore, the conversion from a rod-like (classic) liquid crystal to a discotic liquid crystal by changing the central metal is the first example in liquid crystals, so far as we know.

Hereupon, we noticed another similar situation at bis(xanthato)nickel(II) [6] (formula 3) and tetrakis(dithioacetato)dinickel(II) [7] (formula 4). Comparing these two complexes, the ligands are not the same but very similar between them, and the central transition metals are the same for each other. Therefore, an investigation of these two nickel complexes substituted by long chains might contribute to liquid crystal chemistry of transition metal complexes.

Hence, we have introduced the long alkyl chains to the two core complexes, bis(xanthato)nickel(II) and tetrakis(dithioacetato)dinickel(II). We wish to report here that each of the tetrakis(*n*-alkyldithiolato)dinickel(II) where *n*-alkyl is *n*-pentyl through *n*-dodecyl, has a monotropic lamella liquid crystalline phase, and that bis(*n*-alkylxanthato)nickel(II) exhibits unique double melting behavior accompanied by an even–odd effect and a monotropic lamella mesomorphism for *n*-nonyl, *n*-undecyl, and *n*-dodecyl groups.

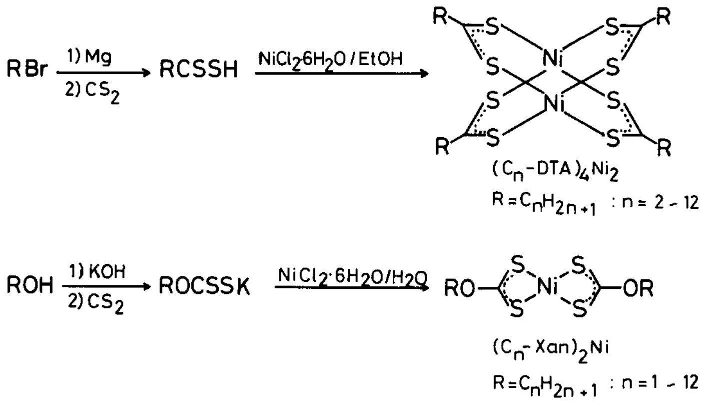
2. Experimental

2.1. *Synthesis*

Syntheses of the present tetrakis(*n*-alkyldithiolato)dinickel(II) complexes (*n*-alkyl: $R = C_nH_{2n+1}, n = 2 \sim 12$: abbreviated as ($C_n$-DTA)$_4Ni_2$) and the bis(*n*-alkylxanthato)nickel(II) complexes (*n*-alkyl: $R = C_nH_{2n+1}, n = 1 \sim 12$: abbreviated as ($C_n$-Xan)$_2$Ni) were carried out according to the routes illustrated in Scheme 1. The tetrakis(*n*-alkyldithiolato)dinickel(II) complexes were prepared by the same manner of C. Bellitto *et al.* [7]. The bis(*n*-alkylxanthato)nickel(II) complexes were prepared by the method of F. Drawert *et al.* [8]. Since the synthetic procedures were almost the same as the case of the octyl substituent, the detailed procedures are presented here only for the complexes, (C_8-DTA)$_4$Ni$_2$ and (C_8-Xan)$_2$Ni.

Tetrakis(n-octyldithiolato)dinickel(II), (C_8-DTA)$_4$Ni$_2$

To a Grignard reagent prepared from *n*-octylbromide (10.0 g, 54 mmol) in THF (40 ml) was added dropwise carbondisulfide (4·4 g, 57 mmol) at 0°C, and the reaction mixture was stirred for an additional hour at this temperature. Then, a dilute aqueous solution of hydrocholoric acid was added to give a red solution. The reaction mixture was extracted with ether, and the organic layer was dried over sodium sulphate. After an evaporation of the ether, to the residue were added 50 ml of ethanol and then nickel(II) dichloride hexahydrate (6·2 g, 26 mmol) in 10 ml of ethanol. After having



Scheme 1. Synthetic routes for tetrakis(*n*-alkyldithiolato)dinickel(II), (C_n-DTA)$_4$Ni$_2$, and bis(*n*-alkylxanthato)nickel(II), (C_n-Xan)$_2$Ni.

stirred for 2 hours at room temperature, a black precipitate was formed, filtered and washed with ethanol to give 2·2 g of the crude complex. The purification was performed by a recrystallization from *n*-hexane to afford 1·3 g of the black plate-like crystals. Yield 11·5 per cent, I.R.(KBr disk, cm^{-1}): 2920, 2850, 1150, 1050, 980, ^{1}H-N.M.R.(CDCl$_3$, TMS): δ_{ppm} = 2·8 (t, 4H, $-CH_2CSS$), 1·3 (m, 24H, $-(CH_2)_6-$), 0·9 (t, 6H, $-CH_3$). The elemental analysis datum was shown in table 1.

Table 1. Elemental analysis data, yields, recrystallization solvents and the crystalline shapes obtained from recrystallization for the complexes, (C_n-DTA)$_4$Ni$_2$.

n	Elemental analysis Found (calcd.) (per cent) C	H	Yield (per cent)	Recrystallization solvent	Crystalline shape
2	26·82(26·78)	3·69(3·75)	24·2	†	Rod-like
3	32·40(32·34)	4·69(4·75)	43·0	*n*-Hexane	Rod-like
4	36·85(36·93)	5·51(5·58)	54·8	*n*-Hexane	Rod-like
5	41·09(40·80)	6·22(6·28)	44·5	*n*-Hexane	Rod-like
6	43·90(44·10)	6·70(6·87)	55·4	*n*-Hexane	Rod-like
7	46·64(46·94)	7·26(7·39)	42·0	*n*-Hexane	Strip-like
8	49·36(49·42)	7·82(7·84)	11·5	*n*-Hexane	Strip-like
9	51·64(51·61)	8·09(8·23)	51·6	*n*-Hexane	Strip-like
10	53·52(53·54)	8·60(8·58)	46·6	*n*-Hexane	Strip-like
11	55·37(55·27)	8·75(8·89)	44·2	*n*-Hexane	Strip-like
12	56·95(56·82)	9·15(9·12)	54·6	*n*-Hexane	Strip-like

† Benzene : *n*-Hexhane = 1 : 1

Bis(n-octylxanthato)nickel (II), (C_8-Xan)$_2$Ni

Potassium hydroxide (2·1 g, 31 mmol) was dissolved in *n*-octanol (20 ml, 127 mmol), and, to this solution, carbondisulphide (2·21 g, 29 mmol) was added dropwise at room temperature with stirring. After 2 hours, the mixture was diluted with 50 ml of distilled water. To this was added an aqueous solution of nickel(II) dichloride hexahydrate (4·0 g, 17 mmol) in 10 ml of water. The reaction mixture was stirred for 2 hrs. A light yellow precipitate was formed and filtered to give 6·7 g of the crude complex. The recrystallization from *n*-hexane to afford 5·4 g of the yellowish brown plate-like crystals. Yield 61·4 per cent, I.R.(KBr disc, cm^{-1}): 2930, 2860, 1260, 910, ^{1}H-N.M.R.($CDCl_3$, TMS): δ_{ppm} = 0·9 (t, 6H, $-CH_3$), 1·3 (m, 24H, $-(CH_2)_6-$), 4·4 (t, 4H, $-OCH_2-$), Electronic spectrum (in chloroform): $\lambda_{max}(\varepsilon)$: 418(2980), 478(1710), 318(30 600), 251(19 000). The elemental analysis datum was shown in table 2.

2.2. *Measurements*

The phase transition behaviours of these complexes were observed by a polarizing microscope equipped with a heating plate controlled by a thermoregulator, Mettler FP80 and FP82, and measured with differential scanning calorimeters, Rigaku Thermoflex TG-D.S.C. and Rigaku Thermoflex D.S.C.-10 A. The X-ray diffraction powder patterns of the phases of these complexes were measured with Cu–K_α radiation, using a Rigaku Geigerflex equipped with a heating plate controlled by a thermoregulator [9]. The infrared spectra were recorded on a JASCO A-302 equipped with a heating apparatus. The time dependence of the molecular weights of the $(C_n\text{-DTA})_4Ni_2$ complexes was observed by using a Colona 117 Molecular Weight Apparatus vapour pressure osmometer. The solvent was chloroform which had been distilled twice before the use.

3. Results and discussion

3.1. *Tetrakis(n-alkyldithiolato)dinickel(II)*, $(C_n\text{-}DTA)_4Ni_2$

3.1.1. *Lamella mesomorphism of tetrakis(n-dodecyldithiolato)dinickel(II)*, $(C_{12}\text{-}DTA)_4Ni_2$

As shown in figure 1(*a*), the complex, $(C_{12}\text{-DTA})_4Ni_2$, was obtained as the strip-like crystals by a recrystallization from *n*-hexane. When the virgin crystals (K) of this complex was heated up from room temperature, it melted into an isotropic liquid (I.L.) at 91·0°C without any phase transitions. On cooling from 95°C to room temperature, the I.L. was transformed into a 'liquid-crystal-like' phase (M) at 67·7°C. This phase gave a broken-fan texture as shown in figure 1 (*b*), and it was fairly stable at room temperature.

The X-ray diffraction powder patterns (figure 2) were measured for the following three states; (*a*): the virgin crystals (K) at room temperature, (*b*): the virgin crystals (K) heated up from room temperature to 80°C and then held at 80°C, and (*c*): the 'liquid-crystal-like' phase (M) obtained by cooling the I.L. from 95°C to room temperature.

Comparing the two patterns of (*a*) and (*b*) in figure 2, they are the same. It indicates that the virgin crystals do not transform with a solid–solid phase transition on heating, which coincides with the microscopic observations mentioned above. Comparing the pattern of (*c*) with those of (*a*) and (*b*), only this powder pattern of the 'liquid-crystal-like' phase (M) lacks the diffraction peak for the high Bragg angles ($2\Theta > 25°$) although the patterns of (*a*) and (*b*) of the K phase show these peaks. This result means that the order of the M phase is reduced from that of the crystal K. On the other hand, each of them, (*a*), (*b*), and (*c*) in figure 2, shows the four strong narrow lines for the low Bragg angles and their spacings are exactly in the ratio 1/2 : 1/3 : 1/4 : 1/5, which is a characteristic of lamella structure. So, it can be thought from these X-ray diffraction powder patterns that the virgin crystal K is a lamella crystalline phase, and that the 'liquid-crystal-like' phase M is a monotropic lamella mesophase.

Table 2. Elemental analysis data, yields, recrystallization solvents, and the colour and the crystalline shapes obtained from recrystallization for the complexes, $(C_n\text{-Xan})_2Ni$.

n	Elemental analysis Found (calcd.) (per cent) C	H	Yield (per cent)	Recrystallization solvent	Colour	Crystalline shape
1	17·67(17·60)	2·21(2·22)	27·8	CCl_4	Brown	Needle-like
2	23·83(23·93)	3·25(3·35)	45·8	EtOH	Dark brown	Plate-like
3	29·46(29·19)	4·18(4·29)	69·2	*n*-Hexane	Dark brown	Strip-like (K_1)
4	33·88(33·62)	4·99(5·08)	73·4	*n*-Hexane	Yellowish brown	Plate-like
5	37·26(37·41)	5·69(5·76)	26·8	*n*-Hexane	Black	Needle-like
6	40·57(40·68)	6·28(6·34)	68·8	*n*-Hexane	Dark brown	Plate-like
7	43·49(43·54)	6·80(6·85)	88·2	*n*-Hexane	Dark brown	Plate-like (K_1)
8	46·28(46·06)	7·29(7·30)	72·3	*n*-Hexane	Yellowish brown	Plate-like (K_1)
9	48·22(48·29)	7·68(7·70)	84·8	*n*-Hexane	Dark brown	Cotton-like (K_1)
10	50·31(50·28)	7·97(8·06)	73·5	*n*-Hexane	Light brown	Plate-like (K_2)
11	52·20(52·07)	8·50(8·38)	55·7	*n*-Hexane	Golden brown	Plate-like
12	53·93(53·69)	8·69(8·67)	83·0	*n*-Hexane	Light brown	Cotton-like

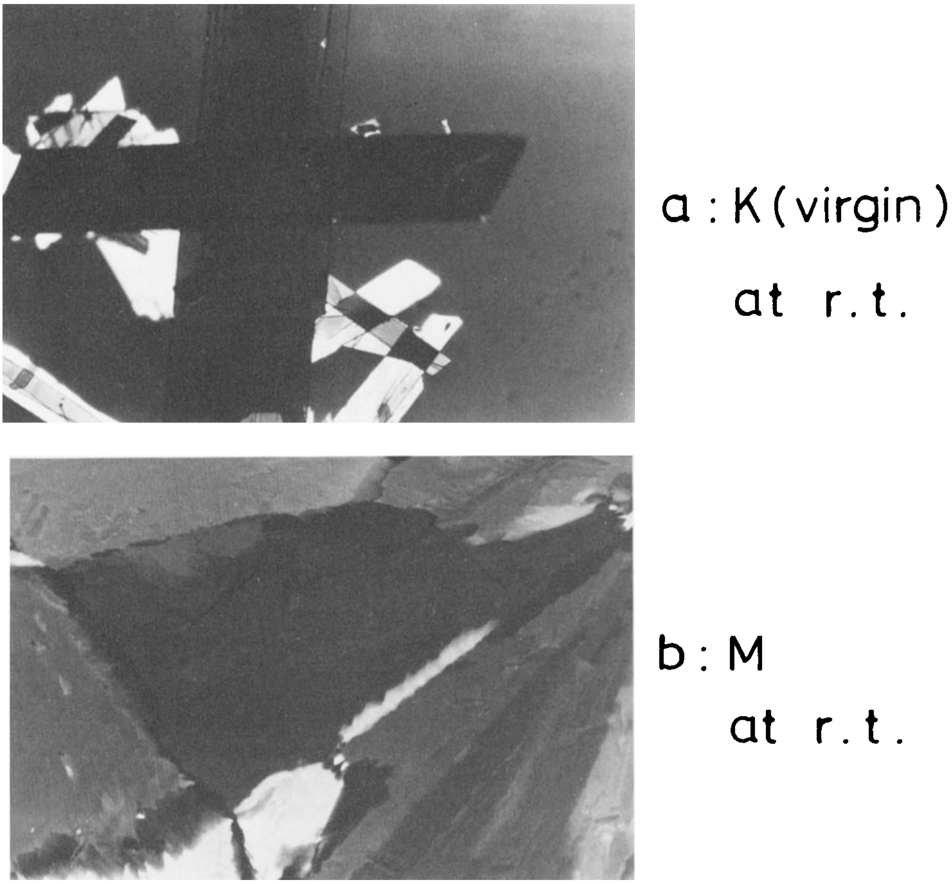


Figure 1. Photomicrographs of the state change of $(C_{12}\text{-DTA})_4Ni_2$: (*a*) the virgin crystals (K), (*b*) the broken-fan texture of the mesophase (M) obtained after having cooled the isotropic liquid from 95°C to 66·9°C.

To obtain more information on the transformation from the K phase to the M phase via the I.L. phase, the infrared spectra were measured. Figure 3 shows the I.R. spectra of this complex, $(C_{12}\text{-DTA})_4Ni_2$, which were measured for a KBr disk sample on the following three phases; (*a*): the virgin crystals (K) at room temperature, (*b*): the isotropic liquid (I.L.) at 95°C, and (*c*): the mesophase (M) obtained by cooling the I.L. from 95°C to room temperature. The temperature-induced changes in the spectra of the alkyl chains can be observed in the region of methylene (CH_2) modes: 700–1500 cm^{-1}. In the I.R. spectrum of the virgin crystals (K) shown in figure 3 (*a*), the components of the CH_2 wagging (1350–1150 cm^{-1}) and the rocking (1170–700 cm^{-1}) band progression [10] are clearly visible. In contrast with this K phase, many band progressions were smeared out both for the I.L. (figure 3 (*b*)) and the M phase (figure 3 (*c*)). The disappearance of the band progression in the I.L. and the M phase indicates that the trans-zigzag conformation of the alkyl chain in both phases is destroyed by the internal rotation of the C–C bonds of the alkyl chain [10]. To be confirmed further this fact, the expanded infrared spectra of this complex were measured in the region of the CH_2 scissoring mode (1500–1400 cm^{-1}) at the various

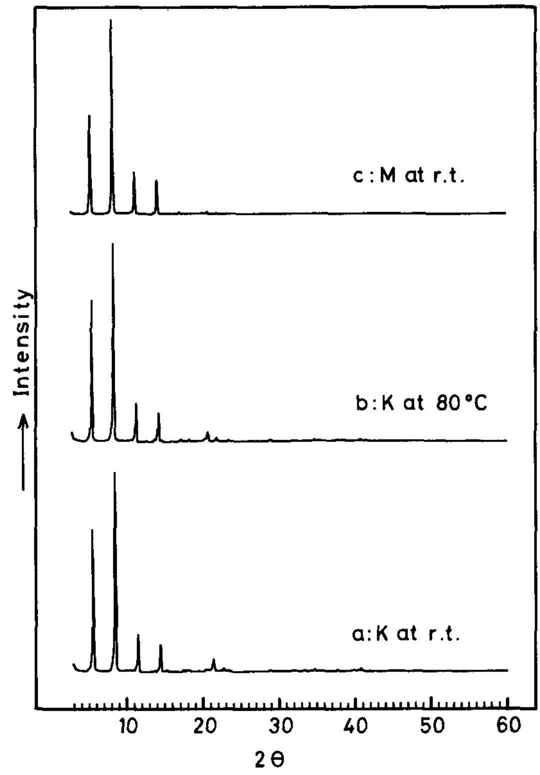


Figure 2. X-ray diffraction powder patterns of $(C_{12}\text{-DTA})_4Ni_2$: (*a*) the virgin crystals (K) at r.t., (*b*) the K crystals heated up to 80°C, (*c*) the mesophase (M) obtained at r.t. having cooled the I.L. from 95°C to r.t.

temperatures as shown in figure 4. It is well-known that the CH_2 scissoring mode reflects well a result of intermolecular interactions between the two alkyl chains [10]. The CH_2 scissoring band could be observed at $1467\,cm^{-1}$ (intense), $1458\,cm^{-1}$ (shoulder), and $1427\,cm^{-1}$ (weak) in the spectra of the virgin crystals (K) at room temperature, 50°C, and 70°C (figure 4(*a*)–(*c*)). In contrast to these spectra, the $1427\,cm^{-1}$ band disappeared and the $1467\,cm^{-1}$ band broadened in both the I.L. and the M phase (figure 4(*d*), (*e*)). Thus, the infrared spectrum of the M phase in the region of the methylene modes is more similar to that of the isotropic liquid (I.L.) than that of the crystal (K).

Therefore, from the microscopic observations, the X-ray diffraction powder patterns, and the I.R. spectra mentioned above, it can be described that the M phase is a monotropic lamella mesophase.

3.1.2. *Is the mesophase of* $(C_{12}\text{-}DTA)_4Ni_2$ *a discotic lamella or a classic lamella (smectic) phase?*

Recently, Ohta *et al.* reported a new mesophase of 'discotic lamella (D_L) phase' in the disk-like copper complexes, bis[1,3-di(*p*-*n*-alkoxyphenyl)propane-1,3-dithionato]-copper(II) [11]. On the other hand, the present complex, $(C_{12}\text{-DTA})_4Ni_2$, has the same molecular structure as that of the disk-like copper(II) dodecanoato complex which exhibits a discotic columnar mesophase (D_h) at the temperatures above 107°C [11].

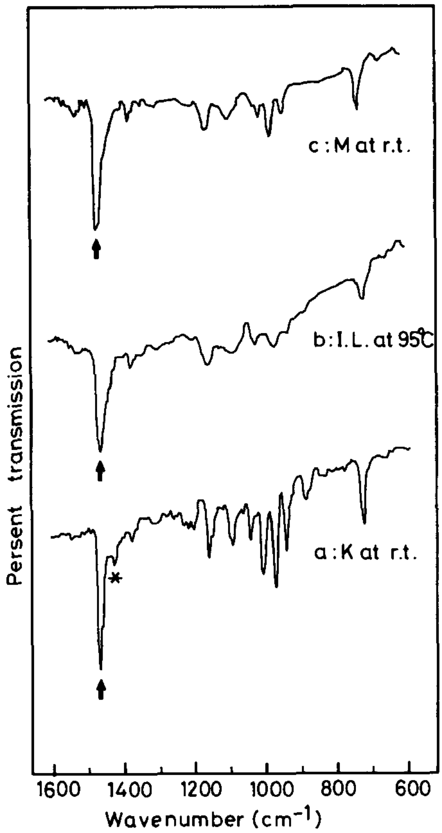


Figure 3. Infrared spectra of (C_{12}-DTA)$_4$Ni$_2$: (*a*) the virgin crystals (K) at r.t., (*b*) the isotropic liquid (I.L.) at 95°C, and (*c*) the mesophase (M) obtained after having cooled the from 95°C to r.t.: KBr disc.

As already mentioned above, the (C_{12}-DTA)$_4$Ni$_2$ complex has not a discotic columnar mesophase but a lamella mesophase. Therefore, the following basic questions must be raised: is the mesophase of (C_{12}-DTA)$_4$Ni$_2$ a discotic lamella (D_L) phase or a classic lamella (smectic, S) phase? Nevertheless, it is very hard to answer this question by constructions of the miscibility diagrams between the present complex and the standard materials of D_L and/or S phases, because the complex decomposes gradually on several heating and cooling cycles in air [6] and because the tetrakis-form (red), (C_{12}-DTA)$_4$Ni$_2$, transforms gradually into the bis-form (yellow), (C_{12}-DTA)$_2$Ni, in a chloroform solution [7].

The time dependence of the molecular weight was observed for the (C_{12}-DTA)$_4$Ni$_2$ and/or (C_{10}-DTA)$_4$Ni$_2$ complexes by using a vapour pressure osmometer. The molecular weight did not indicate a constant value and it gradually decreased from the value of the tetrakis-form with time after the chloroform solution of (C_{10}-DTA)$_4$Ni$_2$ had been prepared. The same phenomenon could be observed also on the electronic spectra of a chloroform solution of (C_{10}-DTA)$_4$Ni$_2$, as shown in figure 5. When the solution was prepared, it was red. After several days, it turned completely to yellow. Figure 5 shows clearly this transformation from the red (tetrakis) form to the yellow

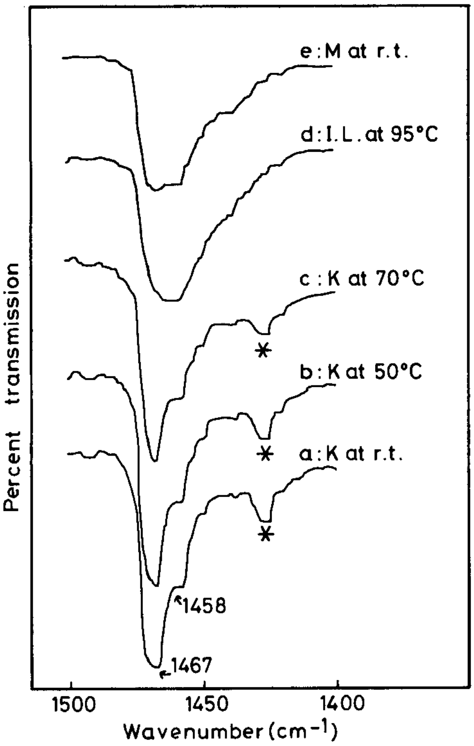


Figure 4. Expanded infrared spectra of $(C_{12}\text{-DTA})_4Ni_2$ in the region of the methylene scissoring band at various temperatures: (*a*) the virgin crystals (K) at r.t., (*b*) K at 50°C, (*c*) K at 70°C, (*d*) the isotropic liquid (I.L.) at 95°C, and (*e*) the mesophase (M) obtained after having cooled the I.L. from 95°C to r.t.: KBr disc.

(bis) form in the chloroform solution with time. The two isosbestic points could be observed at 306 and 379 nm. The red tetrakis-form has two λ_{max} (absorbance) at 279 nm (0·79) and 324 nm (0·49) in the region of 250–400 nm. With time, the 279 nm band absorbance decreased and, on the other hand, the 324 nm band absorbance increased. The ratios of the to absorbance, $A_{279-282}/A_{324-328}$, were 1·62 after 10 min and 0·87 after 6 hours.

The virgin crystals (K) were heated up to 95°C on a hot plate to melt them, and then the fresh melt was quickly taken out into room temperature. The sample was solved in chloroform and then the electronic spectrum of this fresh melt was immediately measured to give the ratio $A_{279-282}/A_{324-328} = 1·33$. The ratio and the shape of this spectrum were very similar to the spectrum after 1 hour in figure 5. Therefore, it can be thought that most of the tetrakis (disc-like)-form remained in the fresh melt although the melt contained a small portion of the bis (rod-like)-form.

Hence, we think from these spectroscopic results that the monotropic lamella mesophase of the present complexes tentatively a discotic lamella (D_L) phase, although it is impossible to establish definitely by the constructions of the miscibility diagrams between the present complex and the standard materials of the D_L phase because it decomposes gradually on several heating and cooling cycles as already mentioned.

3.1.3. *Effect of the alkyl chain length on the mesomorphism of the* $(C_n\text{-}DTA)_4Ni_2$ *complexes*, ($n = 1 \sim 12$)

It was reported by C. Bellitto *et al.* [7] that tetrakis(dithioacetato)dinickel(II), $(C_1\text{-DTA})_4Ni_2$, is stable up to 126°C and decomposes at higher temperatures several without melting. We have synthesized here a series of $(C_n\text{-DTA})_4Ni_2$ ($n = 2 \sim 12$) complexes. It was found that the two complexes, $(C_2\text{-DTA})_4Ni_2$ and $(C_3\text{-DTA})_4Ni_2$, decompose at their melting points, and that the longer chain substituted complexes in $(C_n\text{-DTA})_4Ni_2$ ($n = 4 \sim 12$) are more stable at their melting points than $(C_2\text{-DTA})_4Ni_2$ and $(C_3\text{-DTA})_4Ni_2$ although they decompose gradually on the several heating and cooling cycles.

In table 3 are summarized the transition temperatures (T_t) and the enthalpy changes (ΔH_t). These transition temperatures are plotted against the number of carbon atoms (n) in the alkyl chains in figure 6. It was found that each of the

Table 3. Phase transition temperatures (T_t) and enthalpy changes (ΔH_t) of the complexes, $(C_n\text{-DTA})_2Ni$, (n = 2–12).

n	$\text{Phase}^a \xrightarrow[\Delta H_t(\text{kJmol}^{-1})]{T_t(^\circ\text{C})} \text{Phase}$
2	$\text{K} \xrightarrow{118.4} \text{I.L. (decomp.)}$
3	$\text{K} \xrightarrow{97.6} \text{I.L. (decomp.)}$
4	$\text{K} \xrightarrow[48.5]{80.0} \text{I.L.}$
5	$\text{K} \xrightarrow[46.7]{79.0} \text{I.L.}$ $\text{I.L.} \xrightarrow{43.1} \text{M}$ $\text{M} \xrightarrow{\text{slow}} \text{K}$
6	$\text{K} \xrightarrow[54.4]{84.4} \text{I.L.}$ $\text{I.L.} \xrightarrow{56.3} \text{M}$ $\text{M} \xrightarrow{\text{slow}} \text{K}$
7	$\text{K} \xrightarrow[58.6]{81.8} \text{I.L.}$ $\text{I.L.} \xrightarrow{54.7} \text{M}$ $\text{M} \xrightarrow{\text{slow}} \text{K}$

Table 3 (*continued*).

n	$\text{Phase}^{a} \xrightarrow[\Delta H_t\,(\text{kJmol}^{-1})]{T_t\,(^{\circ}\text{C})} \text{Phase}$
8	$\begin{tikzcd} \text{K} \arrow[rr, "85.0", "69.0"'] & & \text{I.L.} \arrow[dl, "55.3"] \\ & \text{M} \arrow[ul, "\text{slow}"] & \end{tikzcd}$
9	$\begin{tikzcd} \text{K} \arrow[rr, "83.1", "80.8"'] & & \text{I.L.} \arrow[dl, "58.0"] \\ & \text{M} \arrow[ul, "\text{slow}"] & \end{tikzcd}$
10	$\begin{tikzcd} \text{K} \arrow[rr, "87.5", "96.7"'] & & \text{I.L.} \arrow[dl, "62.4"] \\ & \text{M} \arrow[ul, "\text{slow}"] & \end{tikzcd}$
11	$\begin{tikzcd} \text{K} \arrow[rr, "87.8", "100"'] & & \text{I.L.} \arrow[dl, "72.5"] \\ & \text{M} \arrow[ul, "\text{slow}"] & \end{tikzcd}$
12	$\begin{tikzcd} \text{K} \arrow[rr, "91.0", "125"'] & & \text{I.L.} \arrow[dl, "67.7"] \\ & \text{M} \arrow[ul, "\text{slow}"] & \end{tikzcd}$

[a] Phase nomenclature: K = crystal, M = mesophase, I.L. = isotropic liquid.

$(C_n\text{-DTA})_4Ni_2$ ($n = 5 \sim 12$) complexes has a monotropic mesophase. The X-ray diffraction powder patterns revealed that each of the virgin crystals for $n = 7 \sim 12$ has a lamella structure, and that each of the monotropic mesophases for $n = 5 \sim 12$ has also a lamella structure (table 4). The mesophase of the complex, $(C_{12}\text{-DTA})_4Ni_2$, was established as a monotropic lamella liquid crystalline phase by the microscopic observation, the X-ray diffraction powder patterns, and the infrared spectra as already mentioned. Each of the textures of the complexes for $n = 5 \sim 11$ exhibits the same broken-fan texture as that of the $(C_{12}\text{-DTA})_4Ni_2$ complex. Their spacings of these lamella mesophases for $n = 5 \sim 12$ are plotted against the number of the carbon atoms (n) in the alkyl chains in figure 7. A good lineality can be observed between their spacings and the number of the carbon atoms (n). The spacings change 1·94 Å per carbon in the alkyl substituent. It corresponds to the value, 1·34 Å, in the first-established discotic lamella (D_L) mesophases of the bis[1,3-di(*p*-*n*-alkoxyphenyl)-butane-1,3-dionato]copper(II) complexes [11].

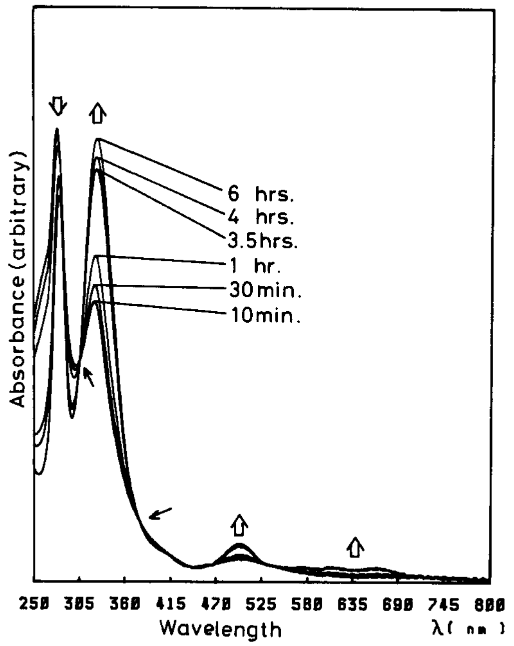


Figure 5. Electronic spectra changes of $(C_{10}\text{-DTA})_4Ni_2$ in chloroform at time intervals after the preparation of the solution. Small arrows indicate the isosbestic points.

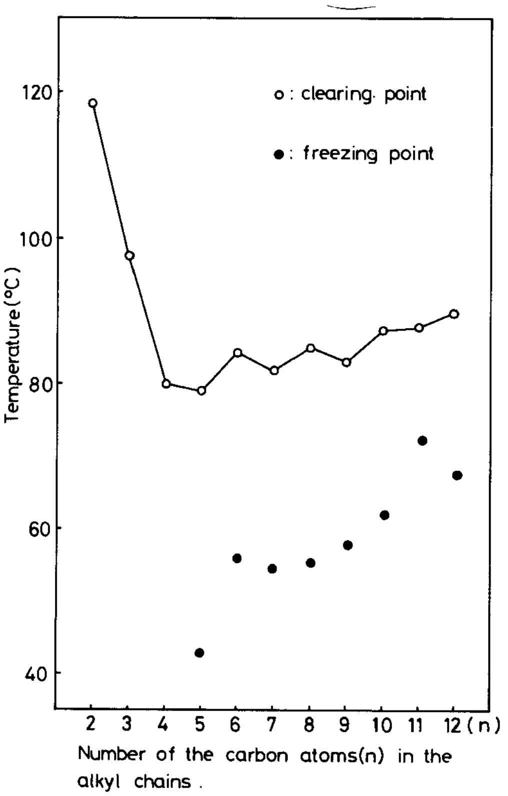


Figure 6. Transition temperatures versus the number of the carbon atoms in the alkyl chains (n) for the $(C_n\text{-DTA})_4Ni_2$ complexes. See table 3.

Table 4. X-ray diffraction data with relative intensities (1 < I/I_1) for the five strongest lines in each solid of (C_n-DTA)$_4$Ni$_2$ complexes.

n		Virgin crystal			Spacing Å I/I_1			Monotropic mesophase		
2	9·19	6·55	4·61	4·12	2·30					
	100	4	5	3	7					
3	10·55	9·83	8·21	5·31	4·31					
	100	39	5	14	6					
4	13·74	8·34	6·80	4·52	2·25	13·79	8·78	8·38	6·93	4·18†
	100	2	15	4	1	100	7	14	10	5
5	15·03	9·05	8·62	7·51	5·00	15·11	7·53	5·03	—	—
	100	4	2	15	4	100	29	8		
6	18·32	9·23	8·36	7·46	6·14	18·68	16·58‡	9·22	8·35	6·16
	100	27	4	2	15	100	17	72	1	39
7	20·29	10·31	6·82	—	—	20·57	10·26	6·85	5·12	—
	100	32	23			100	60	46	2	
8	22·68	11·17	7·47	5·59	—	22·20	11·11	7·44	5·58	—
	100	41	35	2		100	37	28	2	
9	24·47	12·24	8·16	6·12	4·89	24·41	12·31	8·20	6·12	4·90
	100	39	43	5	2	100	45	37	5	2
10	26·11	13·08	8·72	6·55	5·24	26·51	13·16	8·76	6·57	5·25
	100	34	35	4	2	100	36	32	4	2
11	28·41	14·20	9·46	7·10	5·68	28·12	14·20	9·54	7·13	5·70
	100	35	40	7	5	100	48	57	9	6
12	—	15·74	10·30	7·67	6·11	—	15·16	10·06	7·53	6·02
		71	100	18	14		96	100	16	11

† This phase is not a mesophase but a crystalline phase.
‡ Shoulder.

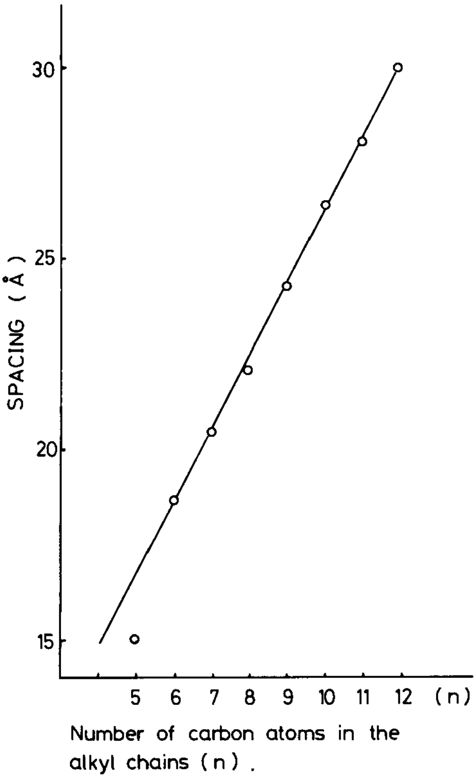


Figure 7. The spacings of the lamella mesophases of the (C_n-DTA)$_4$Ni$_2$ (n = 5 – 12) complexes versus the number of the carbon atoms in the alkyl chains (n). See table 4.

3.2. *Bis(n-alkylxanthato)nickel(II)*, *(C_n-Xan)$_2$Ni* (*n = 1 ~ 12*)

A series of the complexes, bis(*n*-alkylxanthato)nickel(II), (C_n-Xan)$_2$Ni (*n* = 1 ~ 12), have been synthesized here. All complexes except for (C_1-Xan)$_2$Ni are stable until the decomposition temperature of them at *c.* 150°C, in contrast with the unstable (C_n-DTA)$_4$Ni$_2$ complexes mentioned above. The transition temperatures (T_t) of the present complexes are summarized in table 5.

3.2.1. *Unique even–odd effect of the melting behavior in (C_n-Xan)$_2$Ni*

Interestingly, each of the complexes of (C_n-Xan)$_2$Ni (*n* = 5, 7, 9, 11) exhibits double (triple) melting behavior via an isotropic liquid, whereas each of the complexes

Table 5. Phase transition temperatures (T_t) of (C_n-Xan)$_2$Ni complexes (*n* = 1 – 12).

n	$\text{Phase}^{a} \xrightarrow{T_t(^\circ C)} \text{Phase}$
1	$K \xrightarrow{\text{ca. } 150} \text{I.L.}^{b}$
2	$K \xrightleftharpoons{138.8} \text{I.L.}^{c}$
3	$K_1 \xrightleftharpoons{\text{ca. } 75} K_2 \xrightleftharpoons{108.4-108.6} \text{I.L.}$
4	$K \xrightleftharpoons{96.4-97.1} \text{I.L.}$
5	$\begin{tikzcd} K_1 \arrow[dr, "65.5"'] & & K_2 \arrow[r, "66.2"] & \text{I.L.} \\ & \text{I.L.} \arrow[ur] & & \end{tikzcd}$
6	$K \xrightleftharpoons{62.6-62.8} \text{I.L.}$
7	$\begin{tikzcd} K_1 \arrow[r, "41.6"] & K_2 \arrow[dr, "65.3"'] & & K_3 \arrow[r, "66.6-66.8"] & \text{I.L.} \arrow[llll, bend left] \\ & & \text{I.L.} \arrow[ur, "\text{slow}"'] & & \end{tikzcd}$
8	$K_1 \xrightleftharpoons{56-59} K_2 \xrightleftharpoons{67.4-67.5} \text{I.L.}$

Table 5 (*continued*)

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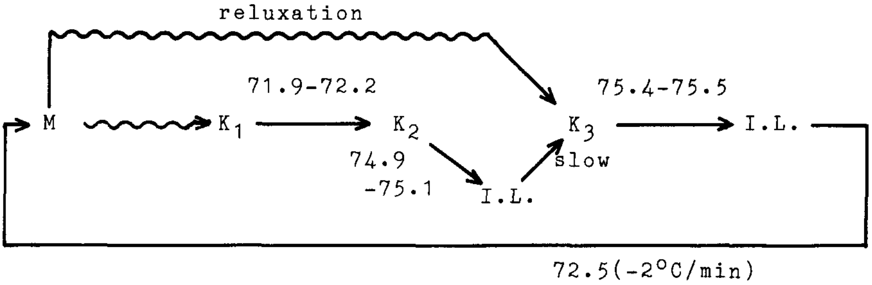

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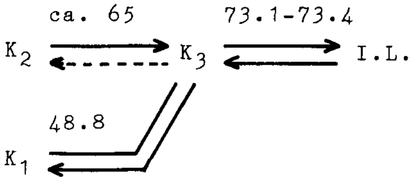

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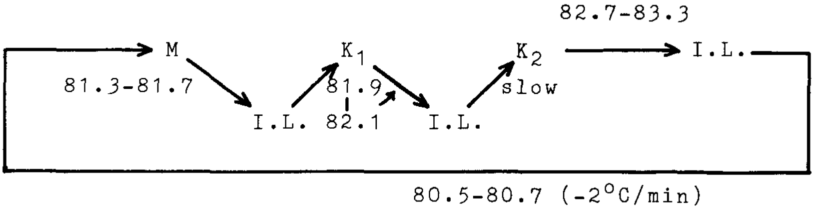

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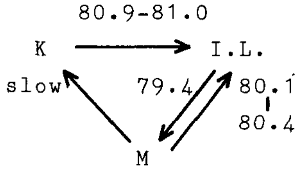

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[a] Phase nomenclature: K = crystal, I.L. = isotropic liquid, M = mesophase.

[b] Decomposition.

[c] Gradual decomposition.

of (C_n-Xan)$_2$Ni (n = 4, 6, 8, 10, 12) shows ordinary single melting behavior. Such unique double melting behavior accompanied by an even–odd effect appears to be the first example of this in the long chain substituted compounds.

3.2.2. *Monotropic mesomorphism in the (C_n-Xan)$_2$Ni complexes (n = 9, 11, 12)*

Each of the present complexes substituted relatively longer alkyl chains, (C_n-Xan)$_2$Ni (n = 9, 11, 12), has a monotropic mesophase. Each of them gives a large broken fan texture, as shown in figure 8. However, the mesophases of (C_9-Xan)$_2$Ni and (C_{11}-Xan)$_2$Ni are unstable and transform relatively fast into their crystalline forms. On the other hand, the mesophase of (C_{12}-Xan)$_2$Ni is fairly stable at temperature higher than 60°C. Hence, the X-ray powder pattern of the mesophase was

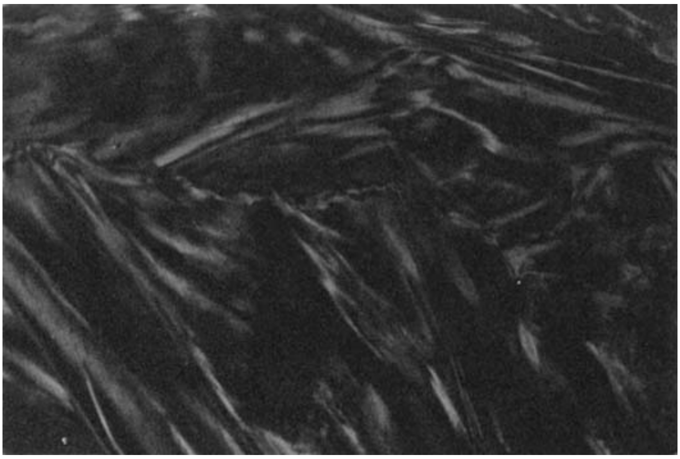

Figure 8. The photomicrograph of the texture of the mesophase of $(C_{12}\text{-Xan})_2Ni$ at 70°C.

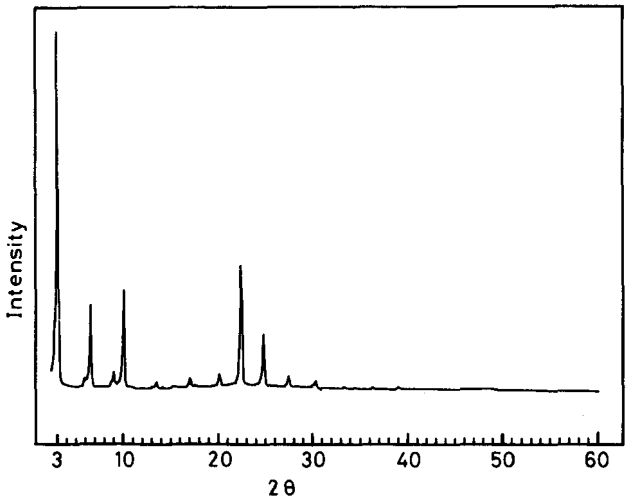

Figure 9. The X-ray diffraction powder pattern of the monotropic mesophase of $(C_{12}\text{-Xan})_2Ni$ at 70°C.

recorded at 70°C as illustrated in figure 9. It can be seen from this pattern in the low Bragg angle region that the mesophase has a lamella structure. Furthermore, there is a very small diffuse element around $2\Theta = 25°$ like a smectic E, G, and H phases. Therefore, each of the present complexes, $(C_n\text{-Xan})_2Ni$ ($n = 9, 11, 12$), has a monotropic smectic mesophase.

4. Conclusion

Two series of the nickel complexes, tetrakis(*n*-alkyldithiolato)dinickel(II) ($(C_n\text{-DTA})_4Ni_2$: $n = 2 \sim 12$) and bis(*n*-alkylxanthato)nickel(II) ($(C_n\text{-Xan})_2Ni$: $n = 1 \sim 12$) have been synthesized. Each of the $(C_n\text{-DTA})_4Ni_2$ complexes has a monotropic lamella mesophase for $n = 5 \sim 12$. The $(C_n\text{-Xan})_2Ni$ complexes exhibit unique double melting behaviour accompanied by an even–odd effect for $n = 4 \sim 12$ and monotropic lamella mesomorphism for $n = 9, 11, 12$.

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