Mesogenic Nickel and Palladium Complexes with Pincer Ligands Derived from Pyridine-2,6-bis(thiocarboxylic) Acid

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Ni complexes with 4-substituted pyridine-2,6-bis(thiocarboxylate) ligands acting as S,N,S-pincers are described. They feature diamagnetic square-planar nickel(II), with three coordination sites taken by the pincer ligand and the fourth coordination position occupied by a 4-substituted pyridine or a 4-substituted biphenyl isocyanide ligand. Only the latter are liquid crystals. The thermal properties of these Ni complexes differ only moderately from those found for similar Pd derivatives. This difference is more important for the compounds with shorter chains. Other changes in the complexes, such as the use of alkylsulfanyl for alkyloxy, or the length of the chain produce an important influence and induce very similar variations for Pd and Ni. Overall Ni shows a somewhat higher tendency to give less ordered (nematic) phases. The use of the newly synthesized chiral 4-substituted pyridine-2,6-bis(thiocarboxylate) acids (E*)-pdtcH_2 (E* = (*R*)-2-butyloxy, (*R*)-2-octyloxy) as pincer ligands leads to chiral square planar Pd and Ni complexes. These chiral complexes show an important lowering in their melting point temperatures compared to their nonchiral S,N,S-pincers homologues and give rise to chiral smectic C (SmC*) and chiral nematic (N*) phases.

Introduction

The extensive research on mesomorphic materials containing transition metals (metallomesogens)[1] has produced a remarkable improvement in the ability to produce these materials using different molecular patterns. There is now a better understanding of the relationship between structure and properties for these materials. However, despite intensive research, we are still far from predicting and controlling their detailed mesomorphic behavior.

Different metals have been incorporated successfully into mesogenic systems. The metal plays an important role in the physical properties of the material. First of all, the metal coordination geometry influences the ligand arrangement, and therefrom the molecular shape, in the molecule core. In this way, different metals offer different possibilities to create molecules with a desired shape. Second, the metal is a center with high electron density and can induce large polarizabilities, which bring about large intermolecular interactions. These give rise often to high melting points and viscosities, but also to the positive effect of large ranges of LC behavior and to the formation of solid glasses retaining the mesophase structure, which can be conveniently used for optical storage.[2,3] In this respect, the thermal properties of calamitic molecules can be noticeably modified by exchanging isostructural metals, while much smaller differences are observed in mesogenic discotic materials, probably because the metal is so buried in the big and more or less symmetric organic environment that its influence is dimmed.[4]

Comparative studies for calamitic liquid crystals of Pd(II) and Pt(II) have been reported for complexes with stilbazoles,[5] isocyanides,[6] nitriles,[7] imines,[2] and azo derivatives,[8] whereas reports of mesomorphic materials containing related complexes of Ni(II) and Pd(II) are scarce. Isostructural alkoxydithiobenzoate[9−11] and dithio-

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(1) (a) Giroud-Godquin, A.-M.; Maitlis, P. M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 375. (b) Espinet, P.; Esteruelas, M. A.; Oro, L. A.; Serrano, J. L.; Sola, E. *Coord. Chem. Rev.* **1992**, *117*, 215. (c) *Inorganic Materials*; Bruce, D., O'Hare, D., Eds.; John Wiley and Sons: Chichester, U. K., 1992; Chapter 8. (d) Hudson, S. A.; Maitlis, P. M. *Chem. Rev.* **1993**, *93*, 3**,** 861. (e) *Metallomesogens*; Serrano, J. L., Ed.; VCH: Weinheim, Germany, 1996. (f) Collinson, S. R.; Bruce, D. W. In *Transition Metal in Supramolecular Chemistry*; Sauvage, J. P., Ed.; John Wiley and Sons: Chichester, U. K., 1999, Chapter 7, p 285. (g) Donnio, B.; Bruce, D. W. *Struct. Bonding* **1999**, *95*, 193.

(2) Buey, J.; Díez, L.; Espinet, P.; Kitzerow, H. S.; Miguel, J. A. *Chem. Mater.* **1996**, *8*, 2375.

(3) Buey, J.; Díez, L.; Espinet, P.; Kitzerow, H. S.; Miguel, J. A. *Appl. Phys. B−Lasers Opt.* **1998**, *66*, 355.

(4) Praefcke, K.; Bilgin, B.; Usol'tseva, N.; Heinrich, B.; Guillon, D. *J. Mater. Chem.* **1995**, *5*, 2257.

(5) Donnio, B.; Bruce, D. W. *J. Chem. Soc., Dalton Trans.* **1997**, 2745.

(6) (a) Kaharu, T.; Tanaka, T.; Sawada, M.; Takahashi, S. *J. Mater. Chem.* **1994**, *4*, 859. (b) Wang, S.; Mayr, A.; Cheung, K. K. *J. Mater. Chem.* **1998**, *8*, 1561.

(7) (a) Bruce, D. W.; Lalinde, E.; Styring, P.; Dunmur, D. A.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1986**, 581. (b) Adams, H.; Bailey, N. A.; Bruce, D. W.; Dunmur, D. A.; Lalinde, E.; Marcos, M.; Ridway, C.; Smith, A. J.; Styring, P.; Maitlis, P. M. *Liq. Cryst.* **1987**, *2*, 381.

(8) Ghedini, M.; Neve, F.; Pucci, D. *Eur. J. Inorg. Chem.* **1998**, 501.

(9) Adams, H.; Albéniz, A. C.; Bailey, N. A.; Bruce, D. W.; Cherodian, A. S.; Dhillon, R.; Dunmur, D. A.; Espinet, P.; Feijoo, J. L.; Lalinde, E.; Maitlis, P. M.; Richardson, R. M.; Ungar, G. *J. Mater. Chem.* **1991**, *1*, 843.

(10) Ohta, K.; Ema, H.; Morizumi, Y.; Watanabe, T.; Fujimoto, T.; Yamamoto, I. *Liq. Cryst.* **1990**, *3*, 311.

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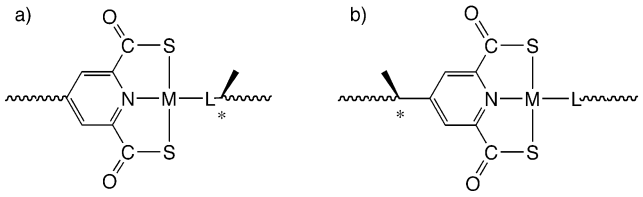
carbamate[12] complexes are liquid crystalline for both Ni and Pd. When dithiolenes are used as ligand, the nickel complexes display enantiotropic mesophases, whereas the palladium derivatives do not show mesomorphism.[13,14] Contrarily, in benzoyloxysalicylaldimine compound the mesomorphic properties observed for palladium disappear completely for nickel.[15]

Although square-planar complexes $[MX_2L_2]$ (M = Pd, Pt, X = halide) are extremely numerous, they often consist of mixtures of isomers. Despite this, some have been used in the synthesis of liquid crystals,[7,16−19] The potentially more interesting less symmetric complexes *trans*-$[MX_2LL']$ are much less common,[20] as they easily undergo symmetrization in addition to isomerization processes (eq 1).

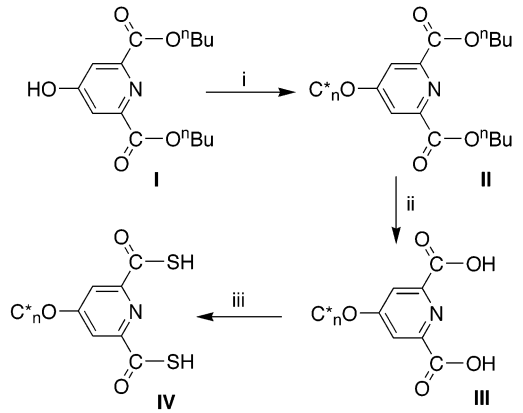
$$\textit{trans}\text{-}[MCl_2LL'] \rightleftharpoons \textit{trans}\text{-}[MCl_2L_2] + \textit{trans}\text{-}[MCl_2L'_2] + \textit{cis}\text{-}[MCl_2L_2] + \textit{cis}\text{-}[MCl_2L'_2] + \textit{cis}\text{-}[MCl_2LL'] \quad (1)$$

A lower symmetry is an interesting property to propitiate a favorable direction for induced polarization associated with the metal center.[21] Moreover, less homogeneous molecular shapes help to reduce the melting points of the compounds.[22] In this respect, dianionic pincer ligands [replacing the role of two Cl and one L, such as in *trans*-$[M(X_2L)L']$ (X_2L = pincer)] are ideal to stabilize a less symmetric situation, as they prevent isomerizations and symmetrizations. We have reported previously Pd(II) mesogens containing O,N,O- and S,N,S-pincer ligands derived from dipicolinic acid and its related dithio acid, with 4-substituted pyridines or isocyanides in the fourth coordination site.[23] Here we report the preparation, characterization, and mesomorphic properties of the isostructural Ni(II) complexes with 4-substituted pyridine-2,6-bis(thiocarboxylate) as the S,C,S-pincer ligand. In the fourth coordination position these Ni(II) complexes have 4-decyloxy-4'-stilbazole (L^1), 4-decyloxy-*N*-(4-pyridylmethylene)aniline (L^2), or 4-isocyano-4'-decyloxybiphenyl (L^3) (see Scheme 1). Comparing their properties with those of their palladium analogues, we find the significant influence of the nature of the metal. To the best of our knowledge, liquid crystals based on nickel(II) isocyanide complexes have not been reported before.

Chart 1



Scheme 1[a]



[a] i: for **g** (*S*)-(+)-2-butanol, for **h** (*R*)-(+)-2-octanol, DEAD, PPh_3, THF; H_2O. ii: KOH, EtOH; HCl. iii: $SOCl_2$, reflux; H_2S, Py, THF; HCl.

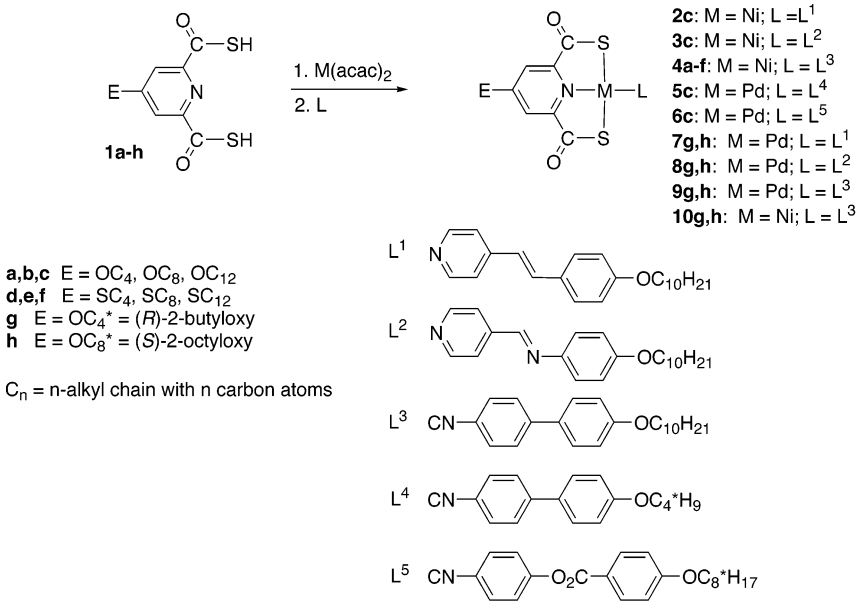
The ferroelectric properties of SmC* phases of metal-containing molecules have been explored in recent years.[24−33] The NLO behavior of metal complexes is also a matter of current interest. High NLO responses have been found for the SmC* phases of nonoptimized (from the NLO point of view) metal-containing molecules.[34−36] For this reason, the observation of N and SmC phases in our Ni and Pd complexes with S,C,S-pincer ligands prompted us to explore the effect of introducing a chiral center in the molecule, aiming to obtain N* and SmC* chiral phases. This purpose has been achieved either by using a chiral monodentate ligand or by introducing a chiral carbon in the chain attached at the pincer ligand (Chart 1). Very different effects are found depending on the method used.

Results and Discussion

Synthesis and Characterization. The chiral tails used in the pincer ligands reported here were the

(11) Bruce, D. W.; Dhillon, R.; Dunmur, D. A.; Maitlis, P. M. *J. Mater. Chem.* **1992**, *2*, 65.
(12) (a) Hoshino-Miyajima, N. *J. Chem. Soc., Chem. Commun.* **1993**, 1442. (b) Hoshino-Miyajima, N.; Matsushita, A.; Miyajima, S. 15th International Liquid Crystal Conference, 1994, Budapest (Hungary).
(13) Giroud, A. M.; Nazzal, A.; Mueller-Westerhoff, U. T. *Mol. Cryst. Liq. Cryst., Lett.* **1980**, *56*, 225.
(14) Mueller-Westerhoff, U. T.; Nazzal, A.; Cox, R. J.; Giroud, A. M. *Mol. Cryst. Liq. Cryst., Lett.* **1980**, *56*, 249.
(15) Bayle, J. P.; Buy, E.; Pérez, F.; Courtieu, J. *Bull. Soc. Chim. Fr.* **1989**, 532.
(16) Maitlis, P. M.; Bruce, D. W.; Dhilon, R.; Dunmur, D. A.; Fanizzi, F. P.; Hunt, S. E.; Le Lagadec, R.; Lalinde, E.; Orr, R.; Rourke, J. P.; Salt, N. J. S.; Atacey, J. P.; Styring, P. *New. J. Chem.* **1990**, *14*, 549.
(17) Adams, H.; Bailey, N. A.; Dhilon, R.; Bruce, D. W.; Dunmur, D. A.; Hunt, S. E.; Lalinde, E. Maggs, A. A.; Orr, R.; Styring, P.; Wragg, M. S.; Maitlis, P. M. *Polyhedron* **1988**, *7*, 1861.
(18) Kaharu, T.; Takahashi, S. *Chem Lett.* **1992**, 1515.
(19) Coco, S.; Díez-Expóxito, F.; Espinet, P.; Fernández-Mayordomo, C.; Martín-Alvarez, J. M.; Levelut, A. M. *Chem. Mater.* **1998**, *10*, 3666.
(20) (a) Rourke, J. P.; Fanizzi, F. P.; Salt, N. J. S.; Bruce, D. W.; Dunmur, D. A.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1990**, 229. (b) Rourke, J. P.; Fanizzi, F. P.; Francesco P.; Bruce, D. W.; Dunmur, D. A.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1992**, 3009.
(21) Espinet, P. *Gold Bull.* **1999**, *32*, 127.
(22) Baena, M. J.; Espinet, P.; Ros, M. B.; Serrano, J. L. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 711.
(23) Espinet, P.; García-Orodea, E.; Miguel, J. A. *Inorg. Chem.* **2000**, *39*, 3645.
(24) Espinet, P.; Etxebarría, J.; Marcos, M.; Pérez, J.; Remón, A.; Serrano, J. L. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1065.
(25) Baena, M. J.; Espinet, P.; Ros, M. B.; Serrano, J. L.; Ezcurra, A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1203.
(26) Baena, M. J.; Barberá, J.; Espinet, P.; Ezcurra, A.; Ros, M. B.; Serrano, J. L. *J. Am. Chem. Soc.* **1994**, *116*, 1899.
(27) Thompson, N. J.; Serrano, J. L.; Baena M. J.; Espinet, P. *Chem. Eur. J.* **1996**, *2*, 214.
(28) Marcos, M.; Serrano, J. L.; Sierra, T.; Giménez, M. J. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1471.
(29) Marcos, M.; Serrano, J. L.; Sierra, T.; Giménez, M. J. *Chem. Mater.* **1993**, *5*, 1332.
(30) Iglesias, R.; Marcos, M.; Serrano, J. L.; Sierra, T.; Pérez-Jubindo, M. A. *Chem. Mater.* **1996**, *8*, 2611.
(31) Athanassopoulou, M. A.; Hiller, S.; Galyametdinov, L. G.; Schweissguth, M.; Haase, W. *Mol. Cryst. Liq. Cryst. A* **1995**, *261*, 29.
(32) Ghedini, M.; Pucci, D.; Scaramuzza, N.; Komitov, L.; Lagerwall, S. T. *Adv. Mater.* **1995**, *7*, 659.
(33) Díez, L.; Espinet, P.; Miguel, J. A.; Ros, M. B. *J. Mater. Chem.* **2002**, *12*, 3694.

Scheme 2



2-butyloxy and the 2-octyloxy groups prepared from the commercial (*S*)-(+)-2-butanol and (*R*)-(−)-2-octanol, respectively. The chiral tails were introduced by means of a nucleophilic substitution, via a Mitsunobu reaction, that takes place with total inversion of the asymmetric center configuration,[37] with dibutyl 4-hydroxypyridine-2,6-dicarboxylate (**I**). The other synthetic steps used to prepare the new chiral pincer ligands (E*)-pdtcH_2 are similar to the procedure described for the achiral ligands (Scheme 1).

The syntheses of **2**−**10** are shown in Scheme 2. They were prepared by acid displacement of acetylacetonate in [M(acac)$_2$] (M = Ni, Pd) with 4-substituted pyridine-2,6-bis(thiocarboxylic) acid, followed by addition of the appropriate stilbazole (L^1), (pyridylmethylene)aniline (L^2), or isocyanides (L^3, L^4, or L^5). Detailed procedures for the 4-substituted pyridine-2,6-bis(thiocarboxylic) acids (E)-pdtcH_2 (E = OC_nH_{2n+1}, SC_nH_{2n+1}), from the commercial chelidamic acid, are available.[23] The complexes are diamagnetic (hence square-planar) orange solids and were isolated in reasonable yields (55−81%) and characterized by satisfactory elemental microanalyses, ^{1}H NMR, and IR. On average, the yields for chiral complexes are somewhat lower that for the achiral ones, due to the higher solubility of the former in the solvents used for purification.

Although the dimeric complex pyridine-2,6-dimethanethiolato nickel(II) has been reported,[38] we failed to obtain good samples of the expected intermediate dimer [Ni_2((E)-pdtc)$_2$]. The materials we obtained gave unsatisfactory C, H, N analysis and featureless, broad NMR spectra, suggesting paramagnetic impurities.

The ^{1}H NMR patterns for **2**-**4** are similar to those found for their homologous palladium derivatives, showing a singlet corresponding to the two equivalent pyridinic hydrogens of the pincer ligands in a monomeric species, as proposed in Scheme 2. The main difference with their palladium analogues is that the chemical shifts observed for the pyridinic protons of the pincer ligand H[3,5] are slightly more shielded for the nickel complexes, while the rest of the signals are almost unmodified. The most prominent feature in their IR spectra is an intense band at ca. 1640 cm^{-1} (15 cm^{-1} higher than for the palladium analogues), assigned to the ν(C═O) vibration of the (E)-pdtc ligands. For the isocyanide complexes **4a**−**f** ν(C≡N) is observed at ca. 2190 cm^{-1}, about 65 cm^{-1} higher than for the free isocyanides, but ca. 25 cm^{-1} lower than for the Pd complexes.

Mesogenic Behavior. The mesomorphic properties of **2**−**10** were determined by a combination of differential scanning calorimetry (DSC) and thermal optical polarized microscopy and are summarized in Table 1 and in Figure 1.

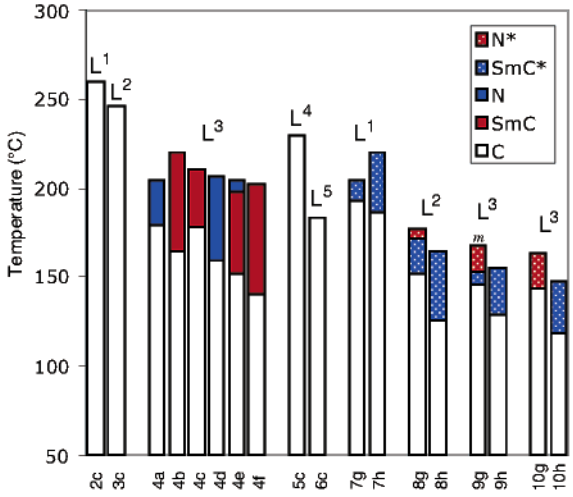


Figure 1. Thermotropic behavior of Ni and Pd complexes with an S,N,S-pincer and a ligand L in the fourth coordination site of a square plane. C, crystal; SmC, smectic C; SmC*, chiral smectic C; N, nematic; N*, chiral nematic; *m*, monotropic transition.

(34) Espinet, P.; Etxebarría, J.; Folcia, C. L.; Ortega, J.; Ros, M. B.; Serrano, J. L. *Adv. Mater.* **1996**, *8*, 745.
(35) Espinet, P.; Etxebarría, J.; Marcos, M.; Pérez-Jubindo, M. A.;. Ros, M. B.; Serrano, J. L. *Mater. Res. Soc. Symp. Proc.* **1995**, *392*, 123.
(36) Ortega, J.; Folcia, C. L.; Etxebarria, J.; Ros, M. B.; Miguel, J. A. *Liq. Cryst.* **1997**, *23*, 285.
(37) Mitsunobu, O. *Synthesis* **1981**, 1.
(38) H. J. Krüger, H. J.; Holm, R. H. *Inorg. Chem.* **1989**, *28*, 1148.

Table 1. Optical, Thermal, and Thermodynamic Data for Compounds 2−10

compd	transition[a]	temp (°C)	ΔH (kJ mol^{-1})
2c	Cr → I[b]	260[c]	−
3c	Cr → I	246.3	37.6
4a	Cr → N	179.1	24.1
	N → I	205.1	0.7
4b	Cr → Cr	94.8	−4.1
	Cr → Cr	161.1	
	Cr → SmC	164.8	32.1[d]
	SmC → I	220.1	10.8
4c	Cr → Cr	56.0	11.2
	Cr → SmC	177.9	20.7
	SmC → I	211.2	8.8
4d	Cr → N	158.8	35.1
	N → I	206.9	1.3
	(SmC → N)[e]	(152.9)	(0.3)
4e	Cr → SmC	151.7	34.7
	SmC → N	198.1	7.9[d]
	N → I	202[c]	
4f	Cr → SmC	139.7	26.4
	SmC → I	202.0	10.5
5c	Cr → I	228.6	42.4
6c	Cr → I	182.5	45.3
7g	Cr → SmC*	193.4	30.1
	SmC* → I[b]	205.4	
7h	Cr → SmC*	187.2	30.8
	SmC* → I	220.2	8.0
8g	Cr → SmC*	152.0	26.1
	SmC* → N*	171.9	0.1
	N* → I	175.1	3.9
8h	Cr → SmC*	126.6	15.5
	SmC* → I	165.4	6.8
9g	Cr → I	166.6	33.7
	(N* → I)[e]	(165.9)	(3.0)
	(SmC* → N*)[e]	(151.1)	(0.5)
9h	Cr → SmC*	128.7	20.4
	SmC* → I	154.6	7.6
10g	Cr → N*	143.3	25.1
	N* → I	163.0	2.0
	(SmC* → N*)[e]	(134.0)	(0.4)
10h	Cr → SmC*	118.1	19.4
	SmC* → I	148.2	7.0

[a] C, crystal; SmC, smectic C; I, isotropic liquid; N, nematic; SmC*, chiral smectic C; N*, chiral nematic. [b] Transition with decomposition. [c] Observed by polarized light microscopy only. [d] Combined enthalpies. Double melting point is observed at 10 °C/min. [e] Monotropic transition.

(*a) Nonchiral Complexes.* The (E)-pdtc ligand with a dodecyloxy chain was chosen first, to help the induction of mesogenic behavior, but the corresponding compound **2c** turned out to be a solid that decomposes before melting. For **3c**, melting of the sample to an isotropic liquid was observed. However, a number of complexes **4** with biphenyl isocyanide as ancillary ligand are enantiotropic liquid crystals and display smectic C or nematic phases. The textures of all the mesophases of the Ni derivatives are quite similar to those of their palladium homologues. The nematic phase was identified by the appearance of droplets, which exhibited typical nematic schlieren and marbled textures, and by the low transition enthalpy to the isotropic liquid. On cooling from the isotropic liquid state, simultaneous occurrence of schlieren and fan-shaped textures was found for the smectic C phase.

A well-known effect is observed upon increasing the length of the chain at the 4-position of the pyridinic ring of the pincer ligand: Compounds **4a** and **4d**, with short chains ($n = 4$), display a nematic phase, whereas for the compounds with longer chains ($n = 8$, 12) a prevalence of the smectic C phase is observed.

Comparing the alkylsulfanyl compounds **4d**−**f** and their oxygen-containing analogues **4a**−**c**, the substitution of E = OC_nH_{2n+1} for E = SC_nH_{2n+1} causes a decrease in the melting points while the clearing temperatures are maintained, thus producing a broader mesogenic range. This interesting favorable influence seems to be quite general, as it has also been noticed for our palladium complexes reported previously [23] and for some alkylsulfanyl-substituted biphenyls with terminal isocyanato substituents.[39]

In addition to a nematic enantiotropic phase, compound **4d** displays also a monotropic SmC phase. The transition from the nematic to the smectic C phase is indicated by the formation of broken fans and typical transition bars above the nematic marbled texture (Figures 2 and 3).[40] A low enthalpy value of ($\Delta H = 0.3$ kJ mol^{-1}) for the transition N−SmC is observed. For **4e**, the nematic mesophase has a very narrow temperature range of existence (4 °C).

Comparison of the Thermal Behavior of the Nickel and Palladium Complexes. Figure 4 shows a direct comparison of the mesogenic properties of isostructural Ni and Pd complexes with the ligands 4-decyloxy-4′-stilbazole (L^1), 4-decyloxy-*N*-(4-pyridylmethylene)aniline (L^2), and 4-isocyano-4′-decyloxybiphenyl (L^3). The change of metal exerts a decisive influence in the complexes with the ligands L^1 and L^2: The nickel compounds **2c** and **3c** are not liquid crystalline, whereas their palladium analogues melt at lower temperatures and are enantiotropic or monotropic, respectively. When the ligand is the biphenyl isocyanide L^3, all the complexes form more stable phases and exhibit better liquid crystal properties than the stilbazole or imine compounds. The differences between Ni and Pd complexes are particularly small, for the derivatives with an alkylsulfanyl group in the 4-position of the pyridyl ring. For those with a 4-alkyloxy chain, the differences are clearly larger for the shorter chains. In general, Ni shows more propensity to give rise to the less ordered nematic phase. All these features are suggestive of a behavior controlled by the polarizability of the molecule along a director coincident with the line L−Pd−N, with more metal influence for short chains in the 4-position of the pyridyl ring. On the other hand, the substitution of O for S as the atom linking these chains to the pyridyl ring seems also to attenuate the effect of the chain. In some cases (e.g complexes with OC_4 in Figure 4) the transition temperatures N−I are lower for the less polarizable Ni, as expected from Maier−Saupe theory,[41] but other cases (e. g complexes with SC_4 in Figure 4) do not show any difference. It has been noted before that metallomesogens often do not conform to this model (ref 1c, p 416).

(*b) Chiral Complexes.* Complexes **5c** and **6c** have the chiral carbon in the terminal chain of the monodentate ligand. They are obtained by coordination of the chiral isocyanides (*R*)-4-(2-butyloxy)-4′-isocyanobyphenyl (L^4) and 4-isocyanophenyl (*R*)-4-(2-octyloxy)benzoate (L^5) to the fragment Pd(E^1-pdtc). Despite **5c** and **6c** having an

(39) Hird, M.; Seed, A. J.; Toyne, K. J.; Goodby, J. W.; Gray, G. W.; Mcdonnell, D. G. *J. Mater. Chem.* **1993**, *3*, 851.
(40) Demus, D.; Richter, L. In *Textures of liquid crystals*, 2nd ed.; VEB: Leipzig, 1980.
(41) Saupe, A.; Maier, W. *Z. Naturforsch* **1961**, *16A*, 816.

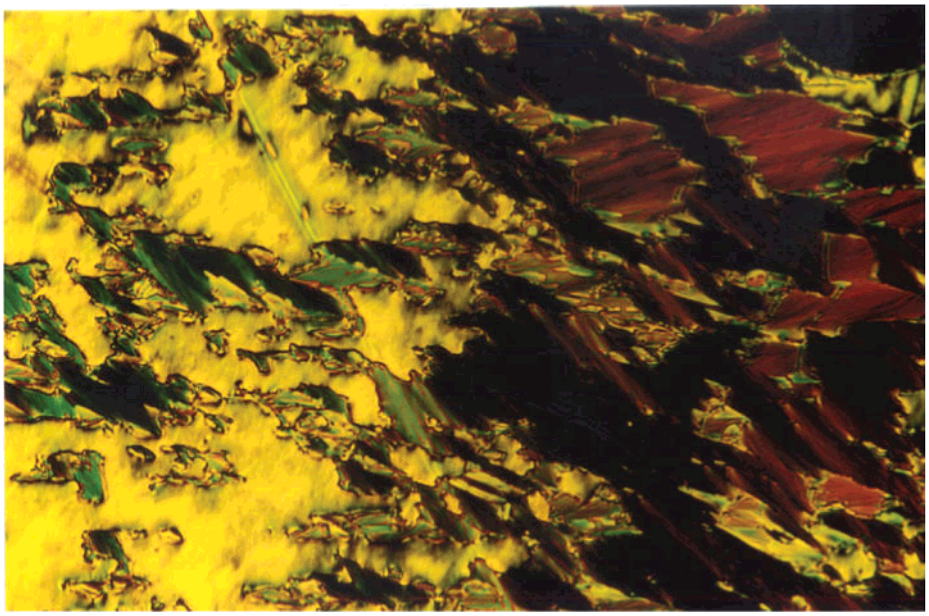


Figure 2. Microphotography of the change N−SmC showing broken fans over a background of *marbled* texture of the N phase. Complex [Ni(C_4S-pdtc)L^3] (**4d**) at 141 °C, crossed polarizers, ×200.

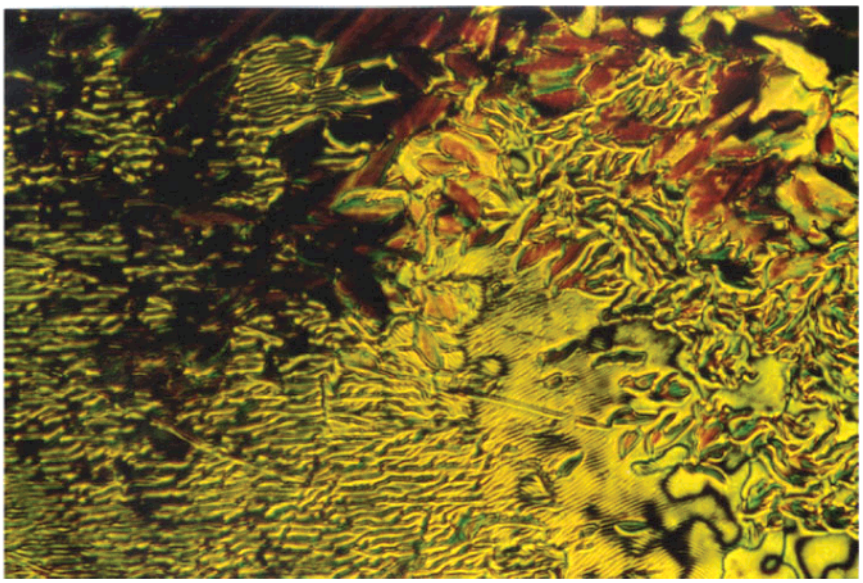


Figure 3. Transition bars appearing in the transition N−SmC. Complex [Ni(C_4S-pdtc)L^3] (**4d**) at 153 °C, crossed polarizers, ×200.

extended conjugated system in the fourth coordination position, which usually gives rise to mesogenic behavior,[23] they are not mesogens. Complexes **7**−**10**, with the chiral carbon in the chain of the pincer, do form chiral complexes with stilbazole L^1, pyridine-imine L^2, or biphenyl isocyanide L^3. It seems that both the perturbing steric effect of the stereocenter and its distance to the rigid core determine very different effects for the two types of complex.[26]

The mesogenic behavior of **5**−**10** is plotted in Figure 1. They are the first case of chiral mesogens designed using a tridentate pincer ligand. Compared to their nonchiral analogues, the chiral carbon in the pincer induces an interesting decrease in the melting points,[42,43] in addition to switching the N and SmC phases to the chiral N* and SmC*. For L = L^2, the stereocenter stabilizes the mesophase (from monotropic to enantiotropic), but the opposite occurs for L^3.

The cholesteric (N*) and chiral smectic C (SmC*) phases displayed by microscopy a *blurred schlieren* texture for the SmC* phase and a typical *fan-shaped* (upon cooling of the isotropic liquid) or oil-streaked texture for the N* phase (Figure 5).

It has been suggested that the presence of two fairly long chains favors the appearance of SmC* phases,[19c] which in fact predominate for compounds with 2-octyl-

(42) Buey, J.; Espinet, P. *J. Organomet. Chem.* **1996**, *507*, 137.

(43) We have found this behavior before. For instance, comparing the nonchiral Pd compounds in ref 42 with their chiral homologues in ref 26, a decrease of about 45 °C is found for the transition temperatures of the chiral complexes.

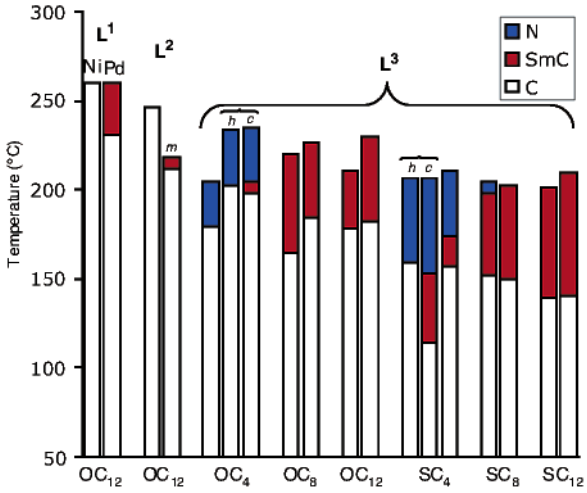


Figure 4. Thermotropic behavior of similar Ni and Pd materials. The left bar in each pair is the Ni compound. When monotropic transitions are present, two bars are shown, one for heating (h) and one for cooling (c). C, crystal; SmC, smectic C; N, nematic.

oxy (derivatives **h**). This phase is also dominant for the complexes **7** and **8** with 4-decyloxy-4′-stilbazole and 4-decyloxy-*N*-(4-pyridylmethylene)aniline respectively, bearing 2-butyloxy. The N* phase is obtained for the shortest chiral chain and is also favored for Ni better than Pd and for 4-isocyano-4′-decyloxybiphenyl better than L^1 or L^2.

Comparing the Pd complexes **7**−**9**, stilbazole leads to higher melting points. The DSC shows that **7g** decomposes, whereas **7h** (with the longest chiral chain) is perfectly stable. The properties of the chiral compounds with biphenyl isocyanide and imine differ less than their nonchiral homologues, and in this case the properties of **8g** with imine L^2 are better than those of **9g** with the isocyanide L^3 (the latter is only monotropic).

Comparing the Pd (**9g** and **9h**) with the Ni (**10g** and **10h**) complexes, again Ni leads to lower melting points and higher stability of N* phases (compare **9g** monotropic with **10g** enantiotropic).

Ferroelectric Properties. The spontaneous polarization (P_s) was determined in the cooling cycle for **10h** between 150 and 103 °C, affording values in the range from 16 to 6 nC cm^{-2}. The maximum P_s value (30 nC cm^{-2}) was obtained at 129 °C, with a response time of 4.5 ms V μm^{-1}. However, the material presents some instability in the electric field, undergoing slow decomposition during the determinations. It is also difficult to align. So the values determined are only approximate.

Pitch and Twisting Power Determination for the Cholesteric Materials. The pitch (p) and helical twisting power ($1/pc$) induced by **8g** and **9g** in mixtures of the Pd complexes (8.5 and 8.9% % in weight) and MLC-6401 (a commercial nematic solvent supplied by Merck) were measured by the Granjean−Cano method,[44] and the results are shown in Figure 6. Compounds **8g** and **9g** show a right-handed helix ($p > 0$) in the range investigated. The pitch value changes noticeably with the monodentate ligand, but both complexes show large pitch values and consequently just a modest helical twisting power. The pitch value of the Ni complex could not be measured using this method, due to the high viscosity of the mixture with the nematic solvent. Solutions with **10g** in different concentrations failed to display disclination lines.

Conclusions

A number of square-planar Ni complexes with 4-substituted pyridine-2,6-bis(thiocarboxylate) ligands acting as S,N,S-pincers have been prepared. Comparison of their thermal properties with those found for similar Pd derivatives reveals that the change of metal exerts only a moderate influence on the mesogenic behavior, this being more important for the compounds with shorter chains. Altogether, Ni seems to have a somewhat higher tendency to give less ordered (nematic) phases. Also, chiral 4-substituted pyridine-2,6-bis(thiocarboxylate) acids (E*)-pdtcH_2 [E* = (*R*)-2-butyloxy, (*R*)-2-octyloxy] have been synthesized and used as pincer ligands for Pd and Ni. The complexes with chiral S,N,S-

Figure 5. Cholesteric texture with oily streaks of [Ni(C*$_4$O-pdtc)L^3] (**10g**) formed at 152 °C on cooling the isotropic liquid (crossed polarizers, ×200).

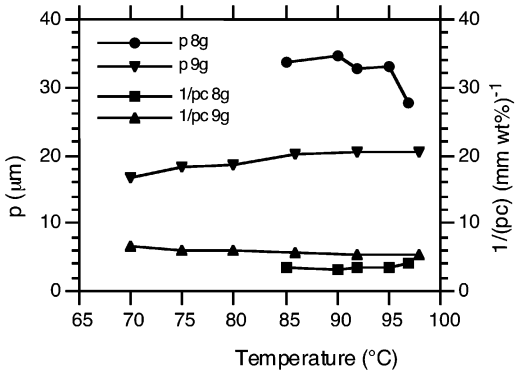


Figure 6. Temperature dependence of the cholesteric helical pitch (p) and the helical twisting power ($1/pc$, c = concentration) of the chiral compound on wt % for a mixture of **8g** (8.5 wt %) and **9g** (8.9 wt %) and the commercial nematic solvent MLC-6401.

pincers show an important lowering in their melting point temperatures, compared to their achiral homologues, and display chiral smectic C (SmC*) and chiral nematic (N*) phases.

Experimental Section

Literature methods were used to prepare [Ni(acac)$_2$],[45] 4-substituted pyridine-2,6-bis(thiocarboxylic) acid,[23] and the ligands L^1,[46]L^2,[47] L^3, [48] and L^4.[49]A sample of L^5 was kindly provided by Dr. S. Coco. Its synthesis is as reported for 4-isocianophenyl 4-*n*-octyloxybenzoate,[6a] but using the Mitsunobu reaction with (*S*)-2-octanol to introduce the (*R*)-2-octyl chain. C, H, N analyses were carried out on a Perkin-Elmer 2400 microanalyzer. All the new compounds gave satisfactory elemental analyses (Table S1, Supporting Information). IR spectra were recorded on a Perkin-Elmer FT-1720X spectrometer using Nujol mulls between polyethylene plates. ^{1}H NMR spectra were recorded on Bruker AC-300 or ARX-300 MHz spectrophotometers. The textures of the mesophases were studied with a Leitz microscope with polarizers equipped with a Mettler FP82HT hot stage and a Mettler FP90 central processor, at a heating rate of approximately 10 °C min^{-1}. Transition temperatures and enthalpies were measured by differential scanning calorimetry, with a Perkin-Elmer DSC-7 operated at a scanning rate of 10 °C min^{-1} on heating. The apparatus was calibrated with indium as standard (156.6 °C, 28.5 J g^{-1}), the samples were sealed in aluminum capsules in air, and the holder atmosphere was dry nitrogen.

Typical preparation procedures and physical data are given below. All analogous ligands and complexes were prepared in the same way.

Dibutyl (*S*)-4-(2-Octyloxy)pyridine-2,6-dicarboxylate (II). Compound **II** was synthesized using the Mitsunobu reaction. To a nitrogen-flushed flask containing 1.00 g (3.38 mmol) of dibutyl 4-hydroxypyridine-2,6-dicarboxylate (**I**),[23] 0.53 mL (3.38 mmol) of (*R*)-2-octanol, and 1.10 g (4.19 mmol) of PPh_3 dissolved in 75 mL of dry THF was added dropwise 0.53 mL (3.38 mmol) of diethyl azodicarboxylate (DEAD) dissolved in 20 mL of THF. The reaction mixture was stirred for 20 h. Water (four drops) was added, and stirring was continued for 1 h. The reaction mixture was evaporated to dryness, and the crude residue was treated with a hexane/ethyl acetate (1/4) mixture and filtered. The filtrate was evaporated, and the resulting product was purified on a silica gel column using hexane/ethyl acetate (1/4) as eluent. Yield: 64%. ^{1}H NMR ($CDCl_3$, δ, ppm): 7.69 (s, 2H, $H^{3,5}$), 4.58 (m, 1H, CH), 4.38 (t, J = 6.8 Hz, 4H, OCH_2), 4.10 (t, J = 6.4 Hz, 2H, OCH_2), 1.90−1.10 (overlapping peaks, 21H, CH_2, CHCH_3), 0.96 (t, 6H, CH_3), 0.85 (m, 3H, CH_3). IR (Nujol, cm^{-1}): ν(C=O) 1734s.

(*S*)-4-(2-Octyloxy)pyridine-2,6-dicarboxylic Acid (III). Compound **III** was synthesized as reported for 4-octyloxypyridine-2,6-dicarboxylic acid.[23] Yield: 94%. ^{1}H NMR ($CDCl_3$, δ, ppm): 7.90 (s, 2H, $H^{3,5}$), 4.76 (m, 1H, CH), 1.90−1.20 (overlapping peaks, 13H, CH_2, CHCH_3), 0.86 (m, 3H, CH_3). IR (Nujol, cm^{-1}): ν(C=O) 1741vs, 1758s.

(*S*)-4-(2-Octyloxy)pyridine-2,6-bis(thiocarboxylic) Acid (IV). Compound **IV** was synthesized as reported for 4-octylsulfanylpyridine-2,6-bis(thiocarboxylic) acid.[23] Yield: 54%. ^{1}H NMR ($CDCl_3$, δ, ppm): 7.61 (s, 2H, $H^{3,5}$), 4.59 (m, 1H, CH), 1.90−1.20 (overlapping peaks, 13H, CH_2, CHCH_3), 0.86 (m, 3H, CH_3). IR (Nujol, cm^{-1}): ν(C=O) 1684vs, ν(S−H) 2520s.

Synthesis of 2c. [Ni(acac)$_2$] (0.03 g, 0.12 mmol) and **1c** (0.05 g, 0.12 mmol) were stirred in toluene (15 mL) under a N_2 atmosphere for 1 h. To the dark red suspension was added 4-decyloxy-4′-stilbazole (0.05 g, 0.15 mmol) and a brick red precipitate formed. After 9 h, the solvent was distilled off and the residue was washed with diethyl ether (3 × 3 mL), filtered, and dried in a vacuum. Yield: 81%. ^{1}H NMR ($CDCl_3$, δ, ppm): 8.61, 7.33 (AA′XX′, 4H, NC$_5H_4$), 7.47, 6.91 (AA′XX′, J = 8.7 Hz, 4H, C$_6H_4$), 7.30, 6.79 (d, 15.8 Hz, 2H, HC=CH), 7.14 (s, 2H, $H^{3,5}$) 4.10 (t, J = 6.4 Hz, 2H, OCH_2), 3.99 (t, J = 6.5 Hz, 2H, OCH_2), 1.79 (m, 4H, CH_2), 1.43 (m, 4H, CH_2), 1.26 (overlapping peaks, 28H, CH_2), 0.88 (m, 6H, CH_3). IR (Nujol, cm^{-1}): ν(C=O) 1632.

3c. Yield: 63%. ^{1}H NMR ($CDCl_3$, δ, ppm): 8.87, 7.76 (AA′XX′, 4H, NC$_5H_4$), 8.42 (s, 1H, HC=N), 7.30, 6.93 (AA′XX′, J = 8.8 Hz, 4H, C$_6H_4$), 7.14 (s, 2H, $H^{3,5}$) 4.10 (t, J = 6.5 Hz, 2H, OCH_2), 3.98 (t, J = 6.6 Hz, 2H, OCH_2), 1.79 (m, 4H, CH_2), 1.43 (m, 4H, CH_2), 1.26 (overlapping peaks, 28H, CH_2), 0.88 (m, 6H, CH_3). IR (Nujol, cm^{-1}): ν(C=O) 1635 m, 1620 vs.

4c. Yield: 61%. ^{1}H NMR ($CDCl_3$, δ, ppm): 7.61, 7.44 (AA′XX′, J = 8.4 Hz, 4H, C$_6H_4$), 7.49, 6.98 (AA′XX′, J = 8.7 Hz, 4H, C$_6H_4$), 7.23 (s, s, 2H, $H^{3,5}$), 4.16 (t, J = 6.5 Hz, 2H, OCH_2), 4.00 (t, J = 6.5 Hz, 2H, OCH_2), 1.81 (m, 4H, CH_2), 1.45 (m, 4H, CH_2), 1.26 (overlapping peaks, 28H, CH_2), 0.88 (m, 6H, CH_3). IR (Nujol, cm^{-1}): ν(C≡N) 2196, ν(C=O) 1639.

4f. Yield: 57%. ^{1}H NMR ($CDCl_3$, δ, ppm): 7.61, 7.44 (AA′XX′, J = 8.5 Hz, 4H, C$_6H_4$), 7.49, 6.97 (AA′XX′, J = 8.8 Hz, 4H, C$_6H_4$), 7.50 (s, 2H, $H^{3,5}$), 3.99 (t, J = 6.5 Hz, 2H, OCH_2), 3.07 (t, J = 7.4 Hz, 2H, SCH_2), 1.76 (m, 4H, CH_2), 1.44 (m, 4H, CH_2), 1.26 (overlapping peaks, 28H, CH_2), 0.88 (m, 6H, CH_3). IR (Nujol, cm^{-1}): ν(C≡N) 2183, ν(C=O) 1646.

5c. Yield: 51%. ^{1}H NMR ($CDCl_3$, δ, ppm): 7.63, 7.54 (AA′XX′, J = 8.5 Hz, 4H, C$_6H_4$), 7.49, 6.97 (AA′XX′, J = 8.6 Hz, 4H, C$_6H_4$), 7.31 (s, 2H, $H^{3,5}$), 4.35 (m, 1H, OCH), 4.18 (t, J = 6.5 Hz, 2H, OCH_2), 1.90−1.10 (overlapping peaks, 25H, CH_2, CHCH_3), 0.99 (t, J = 7.4 Hz, 3H, CH_3), 0.87 (t, J = 6.4 Hz, 3H, CH_3). IR (Nujol, cm^{-1}): ν(C≡N) 2214, ν(C=O) 1623, 1633.

6c. Yield: 76%. ^{1}H NMR ($CDCl_3$, δ, ppm): 8.10, 7.60 (AA′XX′, J = 8.8 Hz, 4H, C$_6H_4$), 7.36, 6.95 (AA′XX′, J = 8.9 Hz, 4H, C$_6H_4$), 7.30 (s, 2H, $H^{3,5}$), 4.49 (m, 1H, OCH), 4.19 (t, J = 6.5 Hz, 2H, OCH_2), 1.90−1.10 (overlapping peaks, 33H, CH_2, CHCH_3), 0.88 (m, 6H, CH_3). IR (Nujol, cm^{-1}): ν(C≡N) 2211, ν(C=O) 1726, 1626.

7h. Yield: 80%. ^{1}H NMR ($CDCl_3$, δ, ppm): 8.45, 7.39 (AA′XX′, J = 6.6 Hz, 4H, C$_6H_4$), 7.48, 6.9 (AA′XX′, J = 8.6 Hz, 4H, C$_6H_4$), 7.34, 6.82 (d, J = 16.2 Hz, 2H, CH=CH), 7.20 (s, 2H, $H^{3,5}$), 4.60 (m, 1H, OCH), 3.97 (t, J = 6.5 Hz, 2H, OCH_2), 1.90−1.10 (overlapping peaks, 29H, CH_2, CHCH_3), 0.87 (m, 6H, CH_3). IR (Nujol, cm^{-1}): ν(C=O) 1628.

8h. Yield: 63%. ^{1}H NMR ($CDCl_3$, δ, ppm): 8.71, 7.86 (AA′XX′, J = 6.7 Hz, 4H, C$_6H_4$), 8.49 (s, 1H, CH=N), 7.33, 6.94 (AA′XX′, J = 8.9 Hz, 4H, C$_6H_4$), 7.34, 6.82 (d, J = 16.2 Hz, 2H, CH=CH), 7.23 (s, 2H, $H^{3,5}$), 4.62 (m, 1H, OCH), 3.99 (t, J

(44) Heppke, G.; Oestreicher, F. *Mol. Cryst. Liq. Cryst. Lett.* **1978**, *41*, 245.
(45) Charles, R. G.; Pawlikowski, M. A. *J. Pys. Chem.* **1958**, *62*, 440.
(46) Bruce, D. W.; Dunmur, D. A.; Lalinde, E.; Maitlis, P. M.; Styring, P. *Liq Cryst.* **1988**, *3*, 385.
(47) Marcos, M.; Ros, M. B.; Serrano, J. L.; Esteruelas, M. A.; Sola, E.; Oro, L.; Barberá, J. *Chem. Mater.* **1990**, *2*, 748.
(48) Benouazzane, M.; Coco, S.; Espinet, P.; Martín-Alvarez, J. M. *J. Mater. Chem.* **1995**, *5*, 441.
(49) Bayón, R.; Coco, S.; Espinet, P. *Chem. Mater.* **2002**, *14*, 3515.

= 6.5 Hz, 2H, OCH_2), 1.90−1.10 (overlapping peaks, 29H, CH_2, CHCH_3), 0.87 (m, 6H, CH_3). IR (Nujol, cm^{-1}): ν(C═O) 1628.

9h. Yield: 40%. ^{1}H NMR ($CDCl_3$, δ, ppm): 7.64, 7.54 (AA′XX′, J = 8.5 Hz, 4H, C_6H_4), 7.51, 6.98 (AA′XX′, J = 8.7 Hz, 4H, C_6H_4), 7.27 (s, 2H, $H^{3,5}$), 4.64 (m, 1H, OCH), 4.00 (t, J = 6.5 Hz, 2H, OCH_2), 1.90−1.10 (overlapping peaks, 29H, CH_2, CHCH_3), 0.87 (m, 6H, CH_3). IR (Nujol, cm^{-1}): ν(C≡N) 2212, ν(C═O) 1628.

10h. Yield: 50%. ^{1}H NMR ($CDCl_3$, δ, ppm): 7.61, 7.44 (AA′XX′, J = 8.5 Hz, 4H, C_6H_4), 7.49, 6.98 (AA′XX′, J = 8.8 Hz, 4H, C_6H_4), 7.19 (s, 2H, $H^{3,5}$), 4.61 (m, 1H, OCH), 3.99 (t, J = 6.5 Hz, 2H, OCH_2), 1.90−1.10 (overlapping peaks, 29H, CH_2, CHCH_3), 0.87 (m, 6H, CH_3). IR (Nujol, cm^{-1}): ν(C≡N) 2193, ν(C═O) 1642, 1625.

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Supporting Information Available: Table S1, including the microanalysis, relevant IR bands, yields, and rotatory power of the E-pdtc and E*-pdtc complexes (in PDF format). This material is available free of charge via the Internet at http://pubs.acs.org.

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