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Rod-like Liquid Crystals of Organic Transition Metal Complexes 3[1]: A Reversible Transition between Dimer Smectic E Phase and Monomer Smectic A Phase in the [N,N′-bis(5-alkylsalicylidene) ethylenediaminato nickel(II) Complexes

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Rod-like Liquid Crystals of Organic Transition Metal Complexes 3[1]: A Reversible Transition between Dimer Smectic E Phase and Monomer Smectic A Phase in the [N,N′-bis(5-alkylsalicylidene) ethylenediaminato]nickel(II) Complexes

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It was found that the [N,N′-bis(5-alkylsalicylidene)ethylenediaminato]Ni(II) (abbreviated as $(C_n\text{-Salen})_2Ni$: n = 6, 12) complexes show two smectic liquid crystalline phases, S_E and S_A. The $S_E \leftrightarrows S_A$ phase transition in the C_{12}-salen)$_2$Ni complex is accompanied by a reversible stretching of the interlayer distances. A dimer S_E-monomer S_A phase transition can be deduced from this phenomenon.

INTRODUCTION

A series of long-chain-substituted complexes, [N,N′-bis(5-alkylsalicylidene)ethylenediaminato]nickel(II), (abbreviated as $(C_n\text{-salen})_2Ni$: n = 6, 12; Figure 1) were prepared and their aggregation properties were investigated by Miyamura *et al.*[2–4] They revealed by using ^{1}H-NMR that these complexes form dimers (shown in Figure 1) in a $CDCl_3$ solution, the same case as in their crystalline states.[2] They deduced that the central core of the complexes has a higher effect on the formation of the dimers than the long alkyl-chains.[4] Since this molecular structure is similar to that of general rod-like liquid crystals, we thought that these complexes would show thermotropic liquid crystalline properties and carried out microscopic observations, X-ray diffraction measurements and DSC for the $(C_6\text{-salen})_2Ni$ and

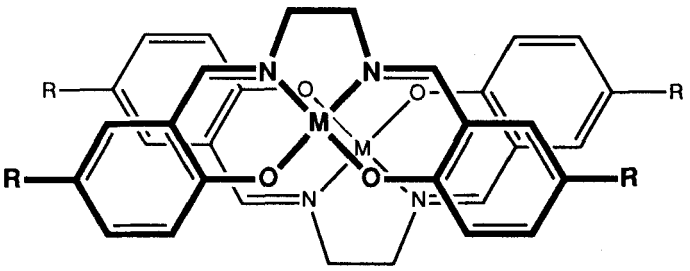

FIGURE 1 Proposed aggregation structure of the $(C_n\text{-Salen})_2Ni$ complex.[2,4]

TABLE I

Phase transition temperatures (T) and enthalpy changes (ΔH) of the $(C_n\text{-Salen})_2Ni$ complexes

Complex	Phase[a] $\xrightarrow[\Delta H(kJ/mol)]{T(^\circ C)}$ Phase
n = 6	$K \xrightarrow[10.6]{126} S_1\ (S_E) \xrightarrow{226} S_2\ (S_A) \xrightarrow{258} I.L.(*)$
n = 12	$K_2 \xrightarrow[16.6]{50} K_3 \xrightarrow[11.1]{116} S_1\ (S_E) \underset{107}{\overset{185}{\rightleftharpoons}} S_2\ (S_A) \xrightarrow{253} I.L.(*)$ K_1

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

* Gradual decomposition.

$(C_{12}\text{-salen})_2Ni$ complexes. As a result, these complexes show thermotropic liquid crystalline phases in accord with expectation: each of these complexes shows a smectic E (S_E) phase and a smectic A (S_A) phase. Very interestingly, the phase transition of $S_E \leftrightarrows S_A$ accompanies a dimer $\leftrightarrows$ monomer transition.

This dimer $S_E \leftrightarrows$ monomer S_A transition is reversible and reproducible. The interlayer distance shrinks for the $S_E \rightarrow S_A$ transition and expands for the $S_A \rightarrow S_E$ transition. We wish to report here on the reversible transition between the dimer S_E phase and the monomer S_A phase.

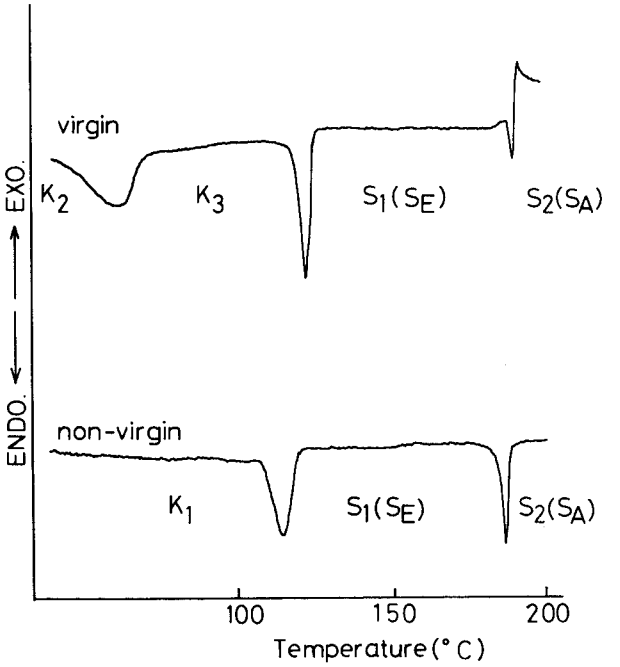

FIGURE 2 DSC thermograms of the virgin and non-virgin samples of the $(C_{12}$-Salen$)_2$Ni complex.

EXPERIMENTAL

These complexes were prepared by Miyamura *et al.*[2–5]

Measurements

Phase transition behaviors of these compounds were observed with a polarizing microscope equipped with a heating plate controlled by a thermoregulator, Mettler FP80 and FP82, and measured with differential scanning calorimeter, Rigaku Thermoflex TG-DSC. The X-ray diffraction measurements on powders were carried out to establish the mesophases. The diffraction patterns were obtained by using a Rigaku Geigerflex with Cu-Kα radiations equipped with a hand-made heating plate controlled by a thermoregulator.[6]

RESULTS AND DISCUSSION

1. Polarizing Microscopic Observations and DSC Measurements

In Table I are summarized the phase transition temperatures and enthalpy changes for the present complexes (n = 6,12) measured by DSC and a polarizing microscope. When the sample of $(C_{12}$-salen$)_2$Ni was heated under a polarizing microscope, it exhibited stickiness with birefringence at ca. 130°C. On further heating

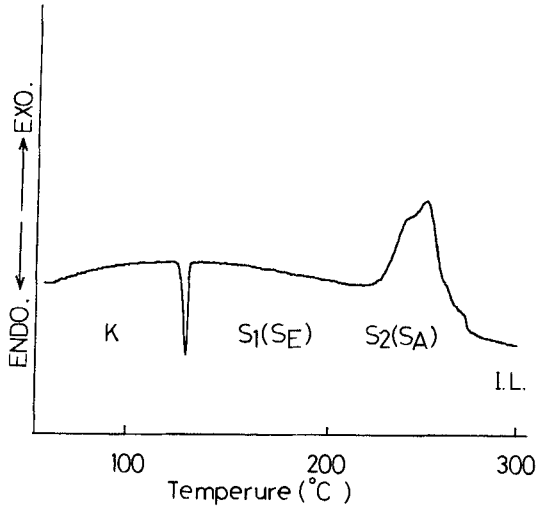

FIGURE 3 DSC thermogram of the virgin sample of the $(C_6\text{-Salen})_2Ni$ complex.

it shrinked suddenly and showed spontaneous fluidity and a focal conic texture at 185°C; it cleared into an isotropic liquid (I.L.) phase at 253°C. When the I.L. phase was cooled down to 250°C, a bâtonnet appeared. On further cooling to ca. 230°C, a mixture of pseudo-isotropic areas and a fan-shaped texture, characteristic of the S_A phase, was observed. On further cooling to 181°C, the fan-shaped texture became a striated one, characteristic of the S_E phase. When the sample was heated up to 190°C, the striated lines disappeared and it returned to the pure fan-shaped texture. The $(C_6\text{-salen})_2Ni$ complex showed the same textures as the $(C_{12}\text{-salen})_2Ni$ complex. Figure 2 shows DSC thermograms of the virgin sample and the non-virgin one of the $(C_{12}\text{-salen})_2Ni$ complex. For the virgin sample of this complex, the K_3 crystals transformed into smectic (S_1) phase at 116°C and it transformed into smectic (S_2) phase at 185°C. The corresponding exothermic peak was, however, hidden by a successive big exothermic peak. On the other hand, for the non-virgin sample, the transition from K_1 crystals to the S_1 phase occured at 107°C and the peak of S_1–S_2 transition was a pure endothermic peak at 185°C. Figure 3 shows a DSC thermogram of the $(C_6\text{-salen})_2Ni$ complex. The crystals (K) transformed into the S_1 phase at 126°C. An exothermic peak was observed for the transition from the S_1 phase to the S_2 phase at 226°C. These thermogravity-analysis (TG) showed no weight loss during the DSC measurements of both the virgin and the non-virgin samples. Therefore, the possibility of a solvent contained in the complex molecule could be excluded. At present, it is not clear why the $(C_n\text{-salen})_2Ni$ complexes (n = 6,12) gave exothermic peaks at the S_1–S_2 transition only for the virgin samples. Further studies are necessary.

2. X-Ray Diffraction Measurements on Powders

It was established by using temperature-dependent X-ray diffraction measurements that the two smectic phases, S_1 and S_2, of the $(C_{12}\text{-salen})_2Ni$ complex are S_A and

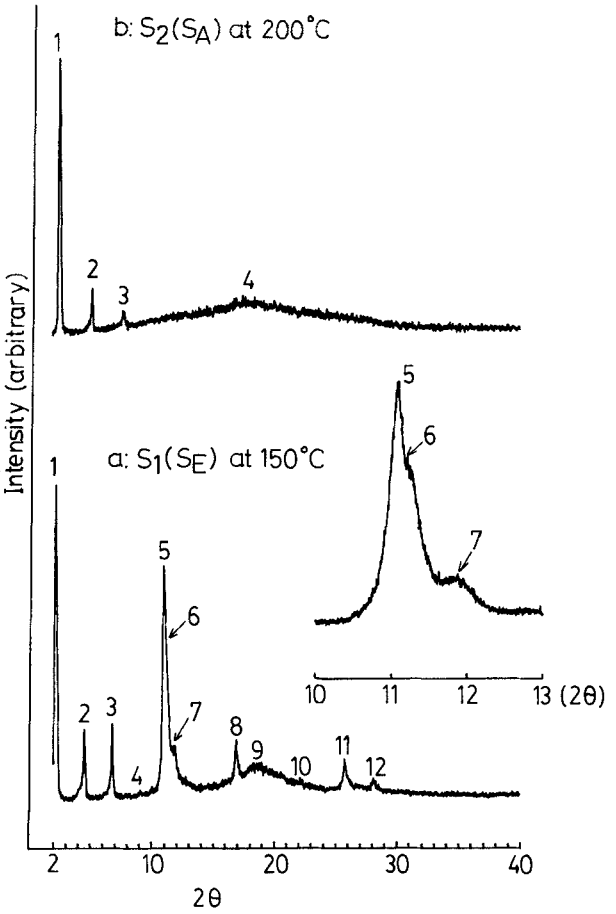

FIGURE 4 X-Ray diffraction powder patterns of the smectic mesophases, S_1 and S_2, in the $(C_{12}$-Salen$)_2$Ni complex.

S_E phases respectively. In Figure 4a and 4b are shown the X-ray diffraction powder patterns of the complex at 150°C and at 200°C, respectively. In Table IIa and IIb are listed all of the spacings observed in these patterns.

Twelve peaks were obtained at 150°C for the $(C_{12}$-salen$)_2$Ni complex as shown in Figure 4a. The peaks of Numbers 1–4 and 6 correspond to a lamellar structure. These peaks could be assigned to Miller indices, (001)–(004) and (005), respectively. The interlamellar distance is 38.3 Å. A diffuse band around $2\theta = 20°$, the peak of No. 9, corresponds to the melting of the alkyl chains. Six other peaks could be assigned using a two-dimensional rectangular lattice. Assuming the peaks of No. 5 and No. 8 to be (110) and (200) reflections respectively, the lattice constants $a = 10.4$ Å, $b = 12.4$ Å were obtained. Using these constants, the reciprocal lattice plane could be drawn as Figure 5. Five peaks agreed with the intersections on the plane, except for the peak of No. 7. Since a smectic liquid crystalline phase having a two-dimensional rectangular lattice is smectic E phase, it could be concluded that this S_1 phase is smectic E phase. This fact is compatible with the result

TABLE II

X-ray diffraction data for the $S_1(S_E)$ and $S_2(S_A)$ mesophases in the $(C_{12}$-Salen$)_2$Ni complex.

a) T = 150°C; S_1 (S_E): a = 10.4Å, b = 12.4Å, c = 38.3Å

Peak No.	Measured lattice spacing(Å)	Calculated lattice spacing(Å)	Miller indices (hkl)	
1	37.6	38.3	(001)	
2	19.1	19.2	(002)	
3	12.8	12.8	(003)	
4	9.66	9.58	(004)	
5	7.97	7.97	(110)	
6	7.88(sh)	7.66	(005)	
7	7.44	-	-	interdimer distance
8	5.19	5.19	(020)	
9	ca. 4.7	-	-	melt of the alkyl chains
10	3.99	3.98	(220)	
11	3.45	3.46	(300)	
12	3.16	3.11	(040)	

b) T = 200°C; S_2 (S_A): c = 33.5Å

Peak No.	Measured lattice spacing(Å)	Calculated lattice spacing(Å)	Miller indices (hkl)	
1	32.8	33.5	(001)	
2	16.7	16.8	(002)	
3	11.2	11.2	(003)	
4	ca. 4.9	-	-	melt of the alkyl chains

of the microscopic observation mentioned above. It is well known that the core complex, [N,N′-bis(salicylidene)ethylenediaminato]copper(II) forms slipped dimers in the crystalline state.[7] Miyamura *et al.* reported that long-alkyl-chain substituted derivatives also form dimers even in $CDCl_3$ solutions.[2–4] Hence, the peak of No. 7, which did not agree with the two-dimensional rectangular lattice, may be regarded as the interdimer distance.

Figure 4b shows the diffraction pattern of the higher temperature smectic (S_2)

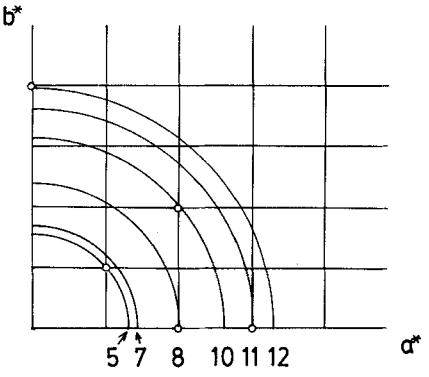

FIGURE 5 Reciprocal lattice of the rectangular system for the S_1 phase of the $(C_{12}\text{-Salen})_2Ni$ complex at 150°C, $a^* = 1/10.4$ Å, $b^* = 1/12.4$ Å.

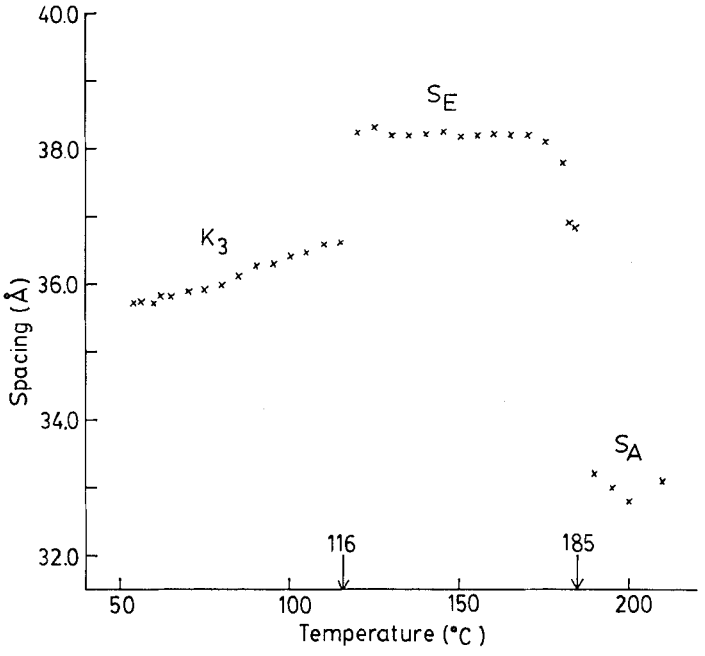

FIGURE 6 Changes of the interlayer distances for the virgin sample of the $(C_{12}\text{-Salen})_2Ni$ complex vs. temperature.

phase at 200°C. It gave three narrow reflections in the low-angle region and their spacings are in a ratio $1:\frac{1}{2}:\frac{1}{3}$, which correspond to the (001), (002) and (003) planes of a lamellar structure. A diffuse band around $2\theta = 20°$ corresponds to the melting of the alkyl chains. From this pattern, it can be concluded that this S_2 phase is a S_A phase or a S_C phase. Since this S_2 phase showed a fan-shaped texture and pseudo-isotropic areas, this phase can be judged to be S_A phase.

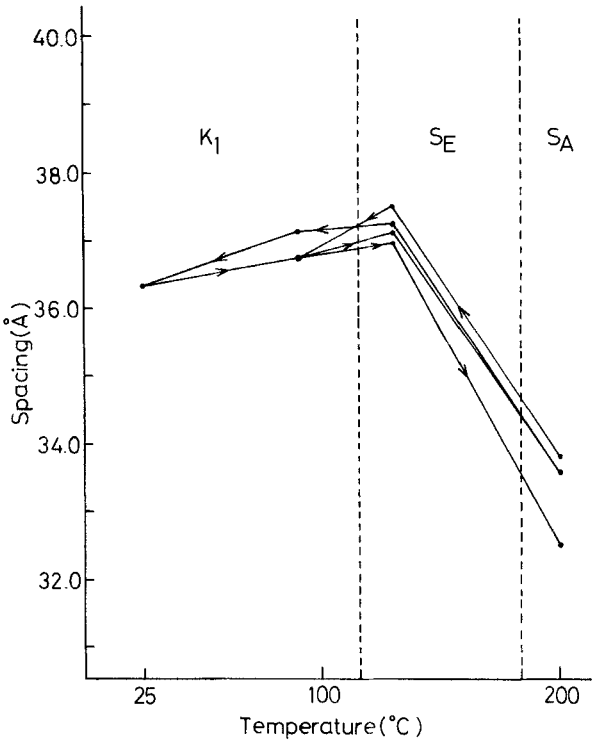

FIGURE 7 Reversible changes of the interlayer distances of the $(C_{12}\text{-Salen})_2Ni$ complex vs. temperature. A virgin sample of this complex was heated and cooled in a series of 200°C (S_A) → 130°C (S_E) → 90°C (K) → 130°C (S_E) → 200°C (S_A) → 130°C (S_E) → 90°C (K) → r.t. (K) → 90°C (K) → 130°C (S_E) → 200°C (S_A).

3. Reversible Stretching of Interlayer Distance with the $S_E \leftrightarrows S_A$ Transition

Figure 6 shows the changes of the interlayer distance of the $(C_{12}\text{-salen})_2Ni$ complex as the temperature rises. These values were calculated from the spacings of (002) and (003) lines at each temperature. The interlayer distance changed sharply at each of the phase transition temperatures of $K_3 \rightarrow S_E$ and $S_E \rightarrow S_A$. When the complex showed the S_E phase, the interlayer distances were constant at about 38 Å. When it showed the S_A phase, they were constant at about 33 Å. Hence, the interlayer distance became about 5 Å shorter at the $S_E \rightarrow S_A$ phase transition.

Furthermore, as shown in Figure 7, the stretching of the interlayer distances could be observed for the heating and cooling cycles. A virgin sample of the $(C_{12}\text{-salen})_2Ni$ complex was heated and cooled in a series of 200°C (S_A) → 130°C (S_E) → 90°C (K) → 130°C (S_E) → 200°C (S_A) → 130°C (S_E) → 90°C (K) → r.t. (K) → 90°C (K) → 130°C (S_E) → 200°C (S_A). These cycles are indicated with arrows in Figure 7. As can be seen in this figure, the interlayer distances extend and shrink reversibly and reproducibly.

Hereupon, we considered the reason why this phenomenon occurs. As mentioned above, these complexes can be considered to form dimers in the S_E phase. Therefore, we thought that this phenomenon was attributable to a dimer-monomer trans-

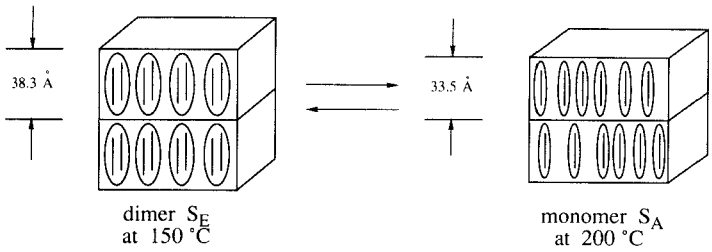

FIGURE 8 Proposed scheme of the transformation between the two smectic mesophases of the $(C_{12}$-Salen$)_2$Ni complex.

formation as illustrated in Figure 8: these complexes formed "slipped dimers" in the S_E phase and became monomeric in the S_A phase in which the slipping would disappear. This will explain the above stretching of the interlayer distances. The value of this slipping, ca. 5 Å, is approximately consistent with that in the crystalline state, ca. 4 Å.[7]

The [N,N′-bis(5-alkoxysalicylidene)ethylenediaminato]Ni(II) complexes which were reported by Paschke *et al.* show only a S_A phase.[8] So, this phenomenon may be characteristic of the present alkyl derivatives.

CONCLUSION

It was found that the [N,N′-bis(5-alkylsalicylidene)ethylenediaminato]Ni(II) complexes showed two smectic liquid crystalline phases, S_E and S_A. The $S_E \leftrightarrows S_A$ phase transition in the $(C_{12}$-salen$)_2$Ni complex is accompanied by a reversible stretching of the interlayer distances. This phenomenon can be ascribed to a dimer S_E–monomer S_A phase transition.

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