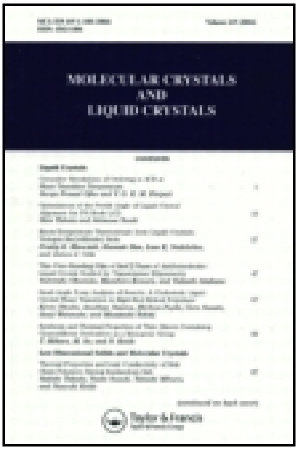

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Mesogenic Properties of Bis(5-Alkoxytropolonato)Metals

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Mesogenic Properties of Bis(5-Alkoxytropolonato)Metals

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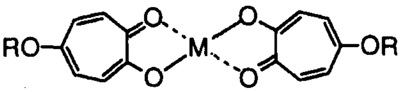
Bis(5-alkoxytropolonato) metallomesogens showed mesogenic properties when the central metal ion was a copper whereas the corresponding zinc complex was not mesogenic. The X-ray diffraction study indicated the mesophases were a smectic B phase and a higher ordered phase such as a crystal B or a smectic G phase.

Keywords: metallomesogens; troponoid liquid crystals; higher ordered smectic phases; X-ray diffraction study

INTRODUCTION

Troponoid liquid crystals with a troponoid ring as a core trend to form smectic layered structures due to the presence of the tropone carbonyl group, which induced the interactions between troponoid rings. We have reported that the monocyclic 2-alkanoyloxy-5-alkoxytropones were monotropically mesogenic[1] and that the characteristic molecular rearrangement, the [1,9] sigmatropy, made the melting point lower[2].

Troponoids have another characteristic point. They form complexes with various metal ions. We recently communicated that bis(5-alkoxytropolonato)copper(II) complexes showed mesogenic properties[3,4] while the corresponding zinc complexes were not mesogenic. This must be dependent on the coordination structure of the complexes; the copper complex has a planar dimeric structure while the zinc complex has a tetrahedral one.



	R	M
1a	$C_{15}H_{31}$	Cu
1b		Zn
1c	$C_{16}H_{33}$	Cu

1a $\mathrm{Cr} \underset{146(16.7)}{\overset{149(21.4)}{\rightleftharpoons}} \mathrm{S_G}^{a} \underset{182(7.8)}{\overset{188(7.6)}{\rightleftharpoons}} \mathrm{B(hex)} \underset{228(36.4)}{\overset{231(36.6)}{\rightleftharpoons}} \mathrm{Iso}$

1b $\mathrm{Cr} \underset{129(2.6)}{\overset{131(4.6)}{\rightleftharpoons}} \mathrm{Cr_1} \underset{166(28.8)}{\overset{173(28.8)}{\rightleftharpoons}} \mathrm{Iso}$

1c $\mathrm{Cr} \underset{142(18.6)}{\overset{146(28.0)}{\rightleftharpoons}} \mathrm{S_G}^{a} \underset{181(8.3)}{\overset{187(7.9)}{\rightleftharpoons}} \mathrm{B(hex)} \underset{227(38.5)}{\overset{229(37.2)}{\rightleftharpoons}} \mathrm{Iso}$

[a] A S_J phase might be possible.

SCHEME 1

On the other hand, the troponoids with secondary alkyl side chains were not mesogenic[3]. Thus, the thermal properties of troponoid metal complexes are sensitive to the central metal ion and the length and the structure of the alkyl chains; the longer alkyl chains enhanced appearance of highly ordered smectic phases and the secondary alkyl chains decreased mesogenic properties. Here, we report the powder X-ray diffraction studies on some metallomesogens.

Synthesis and Thermal Behavior

A methanol solution of 5-alkoxytropolones[1] and copper acetate was stirred to form complexes. The precipitates were collected and washed with solvent. The mesogenic properties were determined by means of measurements of differential scanning calorimetry and polarized optical microscopy and X-ray powder diffraction study. The structure of the complexes and the phase transition temperatures and enthalpy changes of the complexes are shown in Scheme 1.

Measurements of the X-ray Diffraction

The X-ray diffraction measurements were carried out with a Rigaku Rint 2100 system using Ni-filtered Cu-Kα radiation at various temperatures. The measuring temperatures were controlled with a Linkam HFS-91 hot stage. The X-ray diffraction measurements are shown in Fig. 1.

RESULTS AND DISCUSSION

Compound **1a** exhibited smectic B (hexatic) and smectic G phases. The natural texture of the smectic B mesophase was obtained on cooling the isotropic liquid. Also, the mosaic and homeotropic textures appeared in the smectic B mesophase as shown in Fig. 2. The homeotropic smectic B state *showed an optical uniaxial conoscopic figure.*

X-Ray powder studies on **1a** in the smectic B range showed sharp reflections (the first, second, third, and fourth order reflections) at the small-angles, which indicate the formation of a smectic layered structure. The smectic B layer spacing obtained from the first order refection is 29.2 Å.

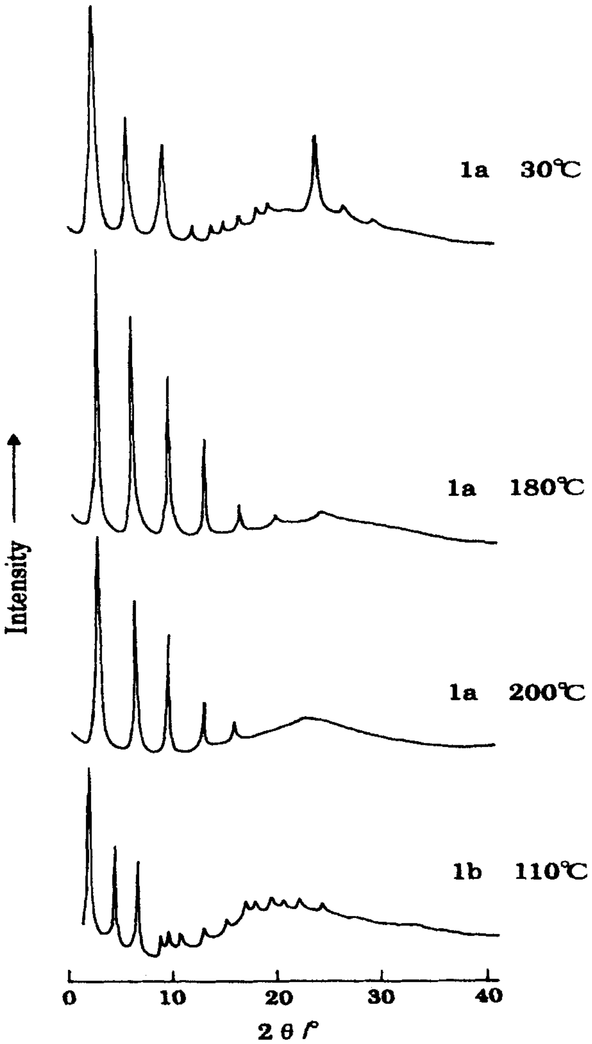


FIGURE 1 X-Ray diffractograms for **1a** at 30 °C (crystal), 180 °C (smectic G), and 200 °C (smectic B), and **1b** at 110 °C (crystal).

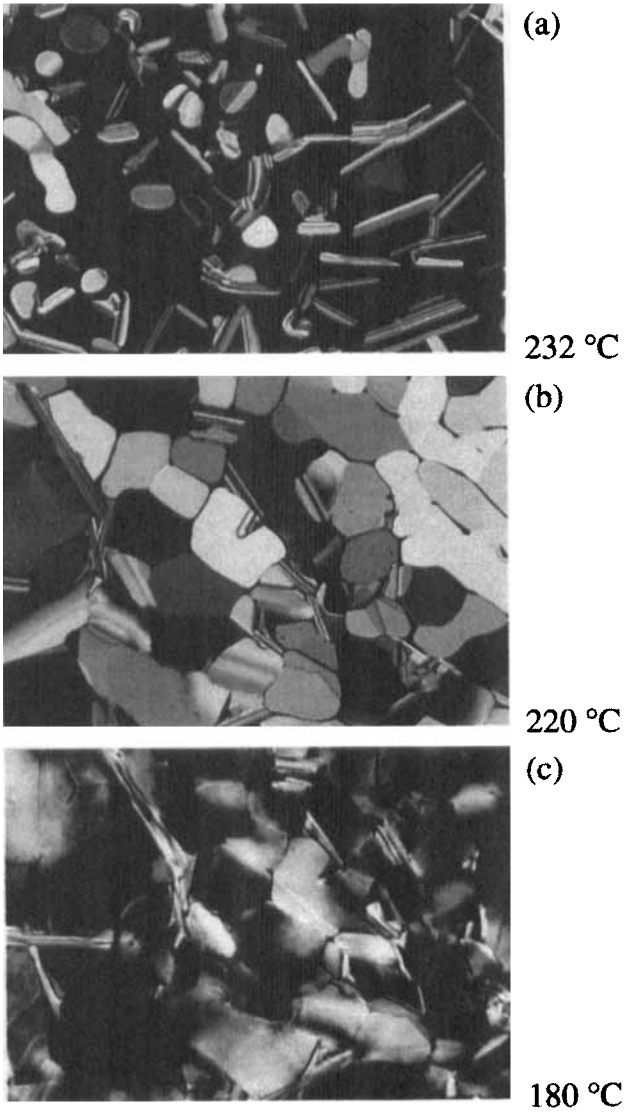


FIGURE 2 Photomicrographs of the liquid crystalline phases of **1a**: 232 °C, I-B (hex) transition (top); 220 °C, mosaic texture of a smectic B phase (middle); 180 °C, mosaic texture of a smectic G phase (bottom).
(See Color Plate IV at the back of this issue)

while the extended molecular length is estimated to be 51 Å. In this case, an interdigitated layered structure, in which long alkyl chains of the complexes are overlapped each other, is proposed as a possible packing model of the smectic B mesophase of **1a** as shown in Fig. 3. The lateral distance between the neighboring molecules is 4.1 Å.

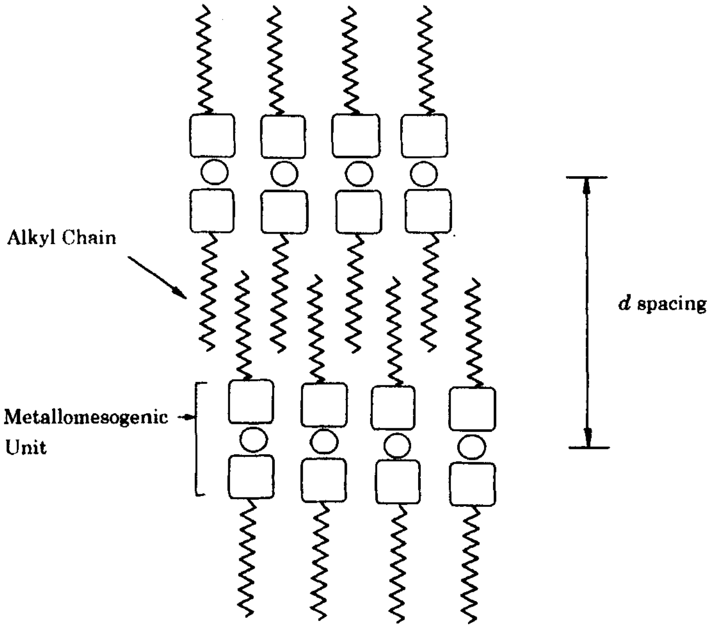


FIGURE 3 Possible packing model of a smectic B phase of **1a** (d=29.2 Å).

In the smectic G state of **1a**, the natural mosaic texture of the smectic B mesophase changed to the broken mosaic texture. On cooling focal conics in the smectic B mesophase with the fluid property, banded focal conics formed in the smectic G phase, which is a very viscous phase. The smectic G state formed on cooling the smectic B mesophase was a highly ordered phase, which showed the X-ray diffraction pattern with the first, second, third, fourth, fifth, and sixth order reflections at the small-angles.

Moreover, the intensity of the X-ray reflections in the smectic G phase with the higher alignment increased when compared to that in the smectic B mesophase. The smectic G layer spacing is 28.4 Å at 180 °C, which is shorter than the smectic B layer spacing (29.2 Å) because, in the smectic G phase, the long axes of molecules tilt with respect to the normal to the layer planes. In this case, the tilt angle in the smectic G phase at 180 °C is estimated to be 13.4 degree. The X-ray studies showed that the smectic layered structure remained unaltered in the crystalline phase formed on cooling the smectic G phase. This stabilization of the smectic G packing is due to interactions between troponoid rings.

Moreover, the microscopic observation and the X-ray studies on **1c** supported that **1c** shows the same phase transitions as **1a**. Compound **1c** exhibited smectic B(hexatic) and smectic G phases. In the smectic B mesophase, the first and second order reflections at the X-ray small-angles were observed. In higher smectic B temperatures, the weak first order reflection was observed at the X-ray small-angle. This indicates that the smectic B alignment was very unstable in the higher temperature. The smectic G orientation, which showed the X-ray diffraction pattern with the first, second, third, fourth, and fifth order reflections at the small-angles, was much higher than the smectic B orientation.

Zinc complex **1b** showed the X-ray scattering peaks exhibiting the crystalline phase. Both the polarizing microscopy and the X-ray diffraction studies indicate that zinc complex is crystalline and do not display the liquid crystal formation. In the crystalline state, **1b** formed a periodic structure (d=43.4 Å), as shown in Fig. 1.

X-Ray diffraction patterns of the smectic complexes exhibited the existence of a higher periodicity in a lamellar-like layered structure. Long alkyl chains and cores of the new smectic metallomesogens produced segregated domains, respectively, such as polar amphiphilic materials. This enhanced liquid crystalline orientation is due to the presence of the tropone carbonyl group, which induced the interactions between troponoid rings.

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