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Discotic Liquid Crystals of Transition Metal Complexes 15[1]: Dimer Discotic Rectangular Ordered Columnar Mesophase in Bis(p-n-hexadecylbiphenylbutane-1,3-dionato)copper(II) Complex

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Discotic Liquid Crystals of Transition Metal Complexes 15[1]: Dimer Discotic Rectangular Ordered Columnar Mesophase in Bis(*p*-*n*-hexadecylbiphenylbutane-1,3-dionato)copper(II) Complex

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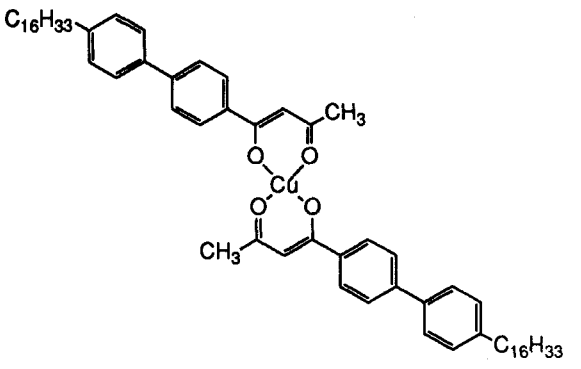
The bis(*p*-*n*-hexadecylbiphenylbutane-1,3-dionato) copper(II) complex shows a dimer discotic rectangular ordered columnar (D_{ro}) mesophase as the same case as the hexadecyloxy derivative. The lattice constants of the two-dimensional rectangular system are a = 47.7 Å, b = 16.8 Å. It was shown that the oxygen atoms in the peripheral alkoxy chains have no effect on the formation of the dimers.

INTRODUCTION

At the present time, it is believed that a discotic liquid crystal has a molecular structure with a rigid core substituted by more than six peripheral chains. However, it has been recently reported in a few papers[2,3] that a molecule having only two peripheral chains shows a discotic liquid crystalline phase. We reported in a previous paper[3] that the bis(*p*-*n*-hexadecyloxybiphenylbutane-1,3-dionato)copper(II) complex forms disk-like dimers which exhibit discotic mesomorphism, although this molecule has an almost rod-like structure with only two peripheral chains. Hereupon, we thought in regard to this molecular structure that the oxygen atoms of alkoxy chains might influence the formation of the dimers; these oxygen atoms might strengthen the interaction between the cores to form the dimers. Therefore, in order to clear the effect of the oxygens on the formation of dimers, we have prepared here a bis(*p*-*n*-hexadecylbiphenylbutane-1,3-dionato)copper(II) complex 1 (Figure 1) and investigated whether it forms its dimers to exhibit the discotic liquid crystalline phase or not. As a result, it was found from X-ray diffraction measurements that this complex also forms dimers to show discotic mesomorphism. Thus, it could be shown that the oxygen atoms have no effect on the formation of



1

FIGURE 1 Formula of bis(*p*-*n*-hexadecylbiphenylbutane-1,3-dionato)copper(II) complex, 1.

TABLE I

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

Phase[a]	T(°C) / ΔH(kJ/mol)	Phase
K[b]	129.5	$D_{r,o}$
$D_{r,o}$	172.5 / 37.3	I.L.

[a] Phase nomenclature; K = crystal, $D_{r,o}$ = discotic rectangular ordered columnar mesophase, and I.L. = isotropic liquid.

[b] Several unidentified phase transitions were observed before melting to the mesophase.

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dimers. In this report, we describe the fact that the complex 1 also shows such a unique dimer discotic columnar rectangular ordered (D_{ro}) liquid crystalline phase.

EXPERIMENTAL

Synthesis

The synthesis of complex 1 was carried out by the same manner reported previously.[3] The crystals are green powder, the same case as the hexadecyloxy derivative. Yield 40.5%. Elemental analysis: Found. (Calcd. for $C_{64}H_{90}O_4Cu$) C 78.17% (77.89) H 9.32% (9.19)

Measurements

The phase transition behavior of this compound synthesized here was observed with a polarizing microscope equipped with a heating plate controlled by a thermoregulator FP80 and FP82, and measured with a differential scanning calorimeter, Rigaku Thermoflex TG-DSC. X-ray diffraction measurements on powders were employed to establish the mesophase. The pattern was obtained using a Rigaku Geigerflex with Cu-Kα radiation equipped with a hand-made heating plate controlled by a thermoregulator.[4]

RESULTS AND DISCUSSION

In Table I are listed the phase transition temperatures and enthalpy changes of complex 1. The liquid crystalline phase of 1 shows a mosaic texture and its is similar to that of the hexadecyloxy derivative reported previously.[3]

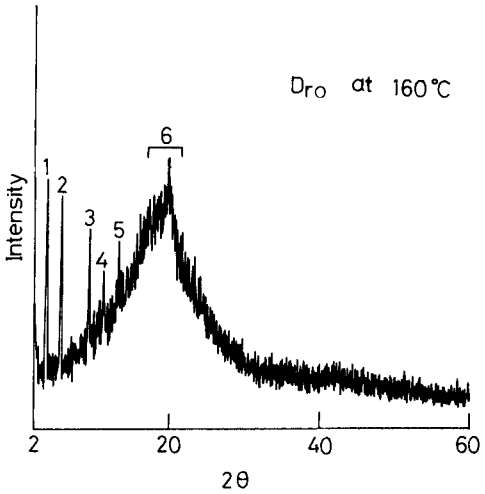

FIGURE 2 X-Ray diffraction powder pattern of complex 1 at 160°C.

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TABLE II

X-ray diffraction data of the mesophase in 1 at 160°C

1: T = 160°C a = 47.7Å, b = 16.8Å

Peak No.	Measured lattice spacing(Å)	Calculated lattice spacing(Å)	Miller indices (hkl)
1	23.86	23.86	(200)
2	15.88	15.88	(110)
3	9.46	9.54	(500) a,a*,b
4	7.87	7.94	(220)
5	6.72	6.87	(420)
6	ca. 4.7	—	— melt of the alkyl chains

a These indexations are not consistent with the extinction rule of a two-dimensional rectangular lattice of C2/m : h+k=2n+1

a* This indexation also is not consistent with the extinction rule of a two-dimensional rectangular lattice of $P2_1/b$: h0: h=2n+1, 0k: k=2n+1

b This reflection corresponds to an interdimer distance.

In Figure 2 is shown the X-ray diffraction pattern of complex 1 at 160°C. Sharp and strong reflections and a diffuse band appear at low and high Bragg angles, respectively. This pattern is a characteristic of mesophases. In Table II are listed all of the spacings observed in this pattern. The five low Bragg-angle peaks could be assigned to (200), (110), (500), (220) and (420) planes in a two-dimensional rectangular lattice, respectively. The diffuse band, peak No. 6 in Figure 2 at ca. $2\theta = 20°$, is attributed to the melting of hexadodecyl chains. The lattice constant values are $a = 47.7$ Å, $b = 16.8$ Å, which are almost the same as those of the hexadecyloxy derivative.[3]

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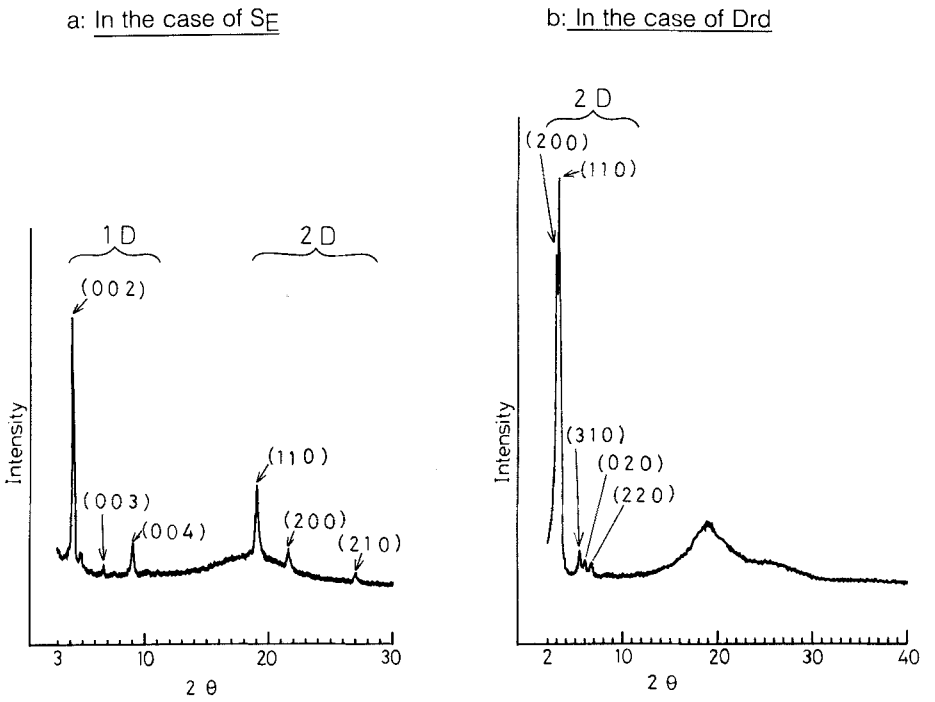

FIGURE 3 Typical X-ray diffraction powder patterns of an S_E phase[6] and a D_{rd} phase[7].

However, two types of mesophase, smectic E and discotic rectangular phases, can exhibit the two-dimensional rectangular structure. Taking account of the long and narrow molecular shape of complex 1, it may be normally judged that the liquid crystalline phase is an S_E phase. In Figure 3 are shown typical X-ray diffraction patterns of an S_E phase (Figure 3a)[6] and a discotic rectangular (D_r) phase (Figure 3b).[7] In the case of smectic E phases, the reflections which come from a two-dimensional structure appear only at high Bragg angles, whereas in the case of D_r phases, these peaks are observed at low Bragg angles. Since the two-dimensionality (2D) peaks appear at low Bragg angles in the present case, it can be deduced that the mesophase of complex 1 is a discotic rectangular phase with formation of dimers being the same as the hexadecyloxy derivative previously reported.[3]

In Figure 4 are shown the extinction rules of two-dimensional rectangular lattices and all low Bragg-angle peaks, except for the third peak, verify these extinction rules for the ($P2_1/b$), (P2/a) and (C2/m). Peak No. 3, which corresponds to the reflection (500), obeys only the extinction rule for the (P2/a). On the other hand, the molecular length of the hexadecyloxy derivative which has been calculated from the C.P.K. model (63–66 Å) cannot be arranged in a lattice with a P2/a symmetry (a = 47.7 Å, b = 16.8 Å). We cannot compact two molecules into the a-axis direction or the b-direction in the (P2/a) lattice. So, the (500) reflection which corresponds to the distance 9.46 Å probably comes from the order of the dimers'

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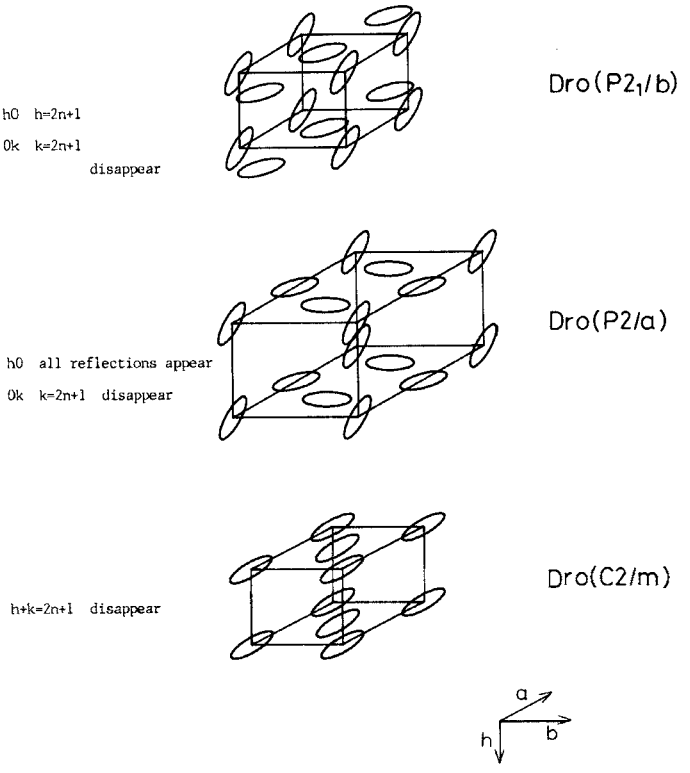

FIGURE 4 Extinction rules in two-dimensional rectangular lattices.

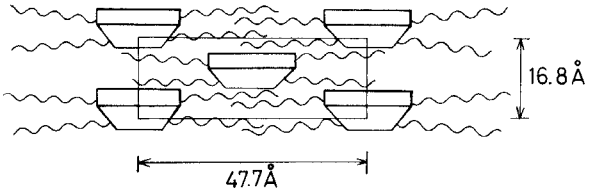

FIGURE 5 Real lattice model for complex 1.

stacking. For the hexadecyloxy derivative this distance has been reported to be 9.40 Å.[3]

We have calculated the number of molecules, Z, in the two-dimensional rectangular ab lattice with the interdimer distance h (a = 47.7 Å, b = 16.8 Å, h = 9.46 Å) by the following equations:

$$Z = \rho VL/M$$

where ρ, the density; V, unit cell volume; L, avogadro's number, and M: the molecular weight. Generally, it is considered that the density of a compound in

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the liquid crystalline state is 0.9 ~ 1.0 g/cm^3.[5] Thereby, the density (ρ) of complex 1 in the liquid crystalline state at 160°C is assumed as 0.95 g/cm^3.

$$V = a \times b \times h$$

$$= 47.7 \times 16.8 \times 9.46 \text{ Å}^3$$

$$= 7581 \times 10^{-24} \text{ cm}^{-3}$$

$$Z = \frac{0.95 \times 7581 \times 10^{-24} \times 6.02 \times 10^{23}}{986.97}$$

$$= 4.4$$

We can deduce that four molecules exist in the *abh* slice of complex 1. Hence, two disks exist in the slice of either ($P2_1/b$) or (C2/m). Furthermore, taking account of the absence of the reflection from the (210) plane, which appears in a rectangular ($P2_1/b$) type, this type can be excluded. Hence, it can be deduced that the type of this two-dimensional rectangular lattice is (C2/m). In Figure 5 is shown the schematic representation of this mesomorphic structure in the D_{ro} (C2/m). Quite recently, it has been reported by Toyne *et al.*[8] that a derivative of complex 1 substituted by a decyl group shows not an enantiotropic discotic columnar phase but a monotropic nematic phase. It should be emphasized that the N phase of the decyl derivative and the D_{ro} phase of the present hexadecyl derivative appear in the same series of complexes 1 only with different alkyl chain lengths.

CONCLUSION

The bis(*p*-*n*-hexadecylbiphenylbutane-1,3-dionato)copper(II) complex shows a dimer discotic rectangular ordered columnar (D_{ro}) mesophase, the same case as the hexadecyloxy derivative. The lattice constants of the two-dimensional rectangular system are a = 47.7 Å, b = 16.8 Å. It was shown that the oxygen atoms in the peripheral alkoxy chains have no effect on the formation of the dimers.

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