Synthesis and Properties of Bis(5-alkoxytropolonato) Metallomesogens

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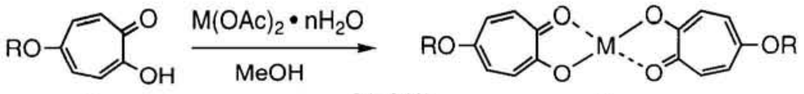
Bis(5-alkoxytropolonato)copper(II) complexes showed mesogenic properties. The corresponding zinc(II) complexes were not mesogenic although they have lower melting points than the copper complexes. The longer alkyl chains enhanced the appearance of highly ordered smectic phases and secondary alkyl chains reduced mesogenic properties.

It is known that tropolone makes complexes with various metal ions. The X-ray crystallographic analysis of the copper(II) complex of tropolone showed that carbon-carbon bond alternation is apparent and the plane of the seven-membered ring makes an angle of 4.9° with the plane of the copper and oxygen atoms.[1] On the other hand, the X-ray crystallographic analysis of tropolone did not show the typical carbon-carbon bond alternation of troponoids, which indicated an almost planar dimeric structure.[2] Recently, we reported that a troponoid ring could work as a core of liquid crystals and sigmatropic troponoids are more mesogenic than the corresponding benzenoids as observed in monocyclic 2-acyloxy-5-alkoxytropones,[3] 5-alkoxy-2-benzyloxytropones,[4] 5-alkylamino-2-(4-alkoxybenzoyloxy)tropones,[5] and 5-alkoxy-2-(4-alkylaminobenzoyloxy)tropones.[6] As an extension of the synthetic works of troponoid liquid crystals, we prepared a new type of metallomesogens with a tropone structure.[7,8]

When 5-alkoxytropolones (**1**)[3] were mixed with copper(II) acetate in methanol, the precipitates[9] formed were collected and washed with solvent to obtain the corresponding copper(II) complexes, whose mesogenic properties were determined by means of measurements of differential scanning calorimetry and polarized optical microscopy and X-ray powder diffraction study.

Bis(5-dodecyloxytropolonato)copper(II) complex (**2a**)



1 34~94% **2**

Table 1. Transition temperatures and enthalpy changes of **2**

	R	M	Transition temp / °C (ΔH / kJ • mol^{-1})
2a	$C_{12}H_{25}$	Cu	$\mathrm{Cr} \underset{167(24.4)}{\overset{170(21.1)}{\rightleftharpoons}} \mathrm{B(cryst)} \underset{183(9.6)}{\overset{191(8.7)}{\rightleftharpoons}} \mathrm{B(hex)} \underset{237}{\overset{237}{\rightleftharpoons}} \mathrm{S_C} \underset{239}{\overset{240}{\rightleftharpoons}} \mathrm{Iso}$
2b	$C_{15}H_{31}$	Cu	$\mathrm{Cr} \underset{146(16.7)}{\overset{149(21.4)}{\rightleftharpoons}} \mathrm{S_G}^{a} \underset{182(7.8)}{\overset{188(7.6)}{\rightleftharpoons}} \mathrm{B(hex)} \underset{228(36.4)}{\overset{231(36.6)}{\rightleftharpoons}} \mathrm{Iso}$
2c		Zn	$\mathrm{Cr} \underset{129(2.6)}{\overset{131(4.6)}{\rightleftharpoons}} \mathrm{Cr_1} \underset{166(28.8)}{\overset{173(28.8)}{\rightleftharpoons}} \mathrm{Iso}$
2d	$C_{16}H_{33}$	Cu	$\mathrm{Cr} \underset{142(18.6)}{\overset{146(28.0)}{\rightleftharpoons}} \mathrm{S_G}^{a} \underset{181(8.3)}{\overset{187(7.9)}{\rightleftharpoons}} \mathrm{B(hex)} \underset{227(38.5)}{\overset{229(37.2)}{\rightleftharpoons}} \mathrm{Iso}$
2e	$C_{18}H_{37}$	Cu	$\mathrm{Cr} \underset{137(20.4)}{\overset{141(24.5)}{\rightleftharpoons}} \mathrm{S_G}^{a} \underset{177(9.4)}{\overset{182(8.9)}{\rightleftharpoons}} \mathrm{B(hex)} \underset{221(35.8)}{\overset{224(36.1)}{\rightleftharpoons}} \mathrm{Iso}$
2f		Zn	$\mathrm{Cr} \underset{69(4.1)}{\overset{120(0.9)}{\rightleftharpoons}} \mathrm{Cr_1} \underset{127(9.4)}{\overset{129(6.0)}{\rightleftharpoons}} \mathrm{Cr_2} \underset{150(27.9)}{\overset{161(25.6)}{\rightleftharpoons}} \mathrm{Iso}$

[a] A S_J phase might be possible.

showed a smectic C phase as well as a smectic B phase and a crystal B while bis(5-pentadecyloxy)-, bis(5-hexadecyloxy)- and bis(5-octadecyloxy)-tropolonatocopper(II) complexes (**2b**, **2d**, **2e**) exhibited a smectic B phase and a highly ordered phase, smectic G or J. The phase transition temperatures and enthalpy changes of **2** are summarized in Table 1. While zinc(II) complexes (**2c** and **2f**) were similarly prepared from 5-pentadecyloxy- and 5-octadecyloxy-tropolones, they were not mesogenic although they have ca. 20 °C lower melting points than the corresponding copper complexes. It can be seen that the coordination geometry of zinc(II) complexes should be tetrahedral although the X-ray crystallographic analysis of the zinc(II) complexes of troponoids has not been analyzed.

X-Ray diffraction measurements on **2b** at 220 °C showed sharp peaks (the first, second, and third order reflections) at small-angles. The smectic layer spacing obtained from the first order reflection is 29.2 Å, while the extended molecular length is estimated to be 51 Å. Moreover, on cooling from an isotropic fluid phase, homeotropic and mosaic natural textures were observed in the smectic mesophase at higher temperature. The conoscopic observation of the homeotropic structure demonstrates that the smectic mesophase has the optical uniaxial orientational ordering. These natural textures indicate that the smectic mesophase should be the smectic B phase. Both the observation of the optical textures and the X-ray powder studies support that, at higher temperature, an interdigitated layered structure, in which long alkyl chains are overlapped each other, is proposed as a possible packing model of **2b**.

The state at lower temperature formed on cooling the smectic B phase was a highly ordered phase, which showed the X-ray diffraction pattern with the first, second, third, fourth, and fifth reflections at small-angles. The smectic layer spacing is 28.4 Å at 180 °C, which is shorter than the smectic B layer spacing. This indicates that the highly ordered phase should be a tilted smectic phase such as a smectic G phase.

Since bistropolonatocopper(II) complexes **2** have high transition temperatures, racemic secondary alkoxy groups were introduced at the 5-position of the troponoid rings to lower melting points. As shown in Table 2, **3** with secondary alkoxy groups exhibited lower melting point than **2** when compared with **2a** and **3c**. Since **3** has the same metallomesogen as smectic **2**, **3** would possess a latent ability of liquid crystal formation. However, the branched methyl groups of **3** would lead to hinder the molecular packing and to lower a latent mesomorphic-isotropic phase transition point. Consequently, the ability of the mesomorphic formation in **3** was reduced and the liquid crystalline phase could not be produced.

Thus, thermal properties of troponoid metal complexes are sensitive to the central metal ion and the length and the structure of the alkyl chain; the longer alkyl chains enhanced appearance of highly ordered smectic phases and secondary alkyl chains decreased mesogenic properties.

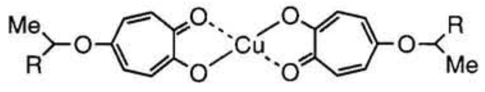


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Table 2. Transition temperatures and enthalpy changes of **3**

	R	Transition temp / °C (ΔH / kJ • mol^{-1})
3a	C_3H_7	Cr $\underset{234(37.7)}{\overset{238(41.2)}{\rightleftharpoons}}$ Iso
3b	C_6H_{13}	Cr $\underset{177(36.6)}{\overset{187(36.2)}{\rightleftharpoons}}$ Iso
3c	$C_{10}H_{21}$	Cr $\underset{44(8.0)}{\overset{48(8.1)}{\rightleftharpoons}}$ Cr_1 $\underset{149(36.3)}{\overset{152(36.5)}{\rightleftharpoons}}$ Iso

References and Notes

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9 The elemental analyses of the compounds reported here are satisfied.