Mesomorphic Properties of Bis(5-alkoxy-2-aminotroponato)coppers and Their *N*, *N*-Dimethyl Derivatives

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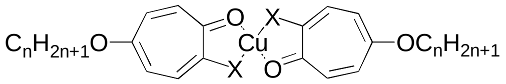
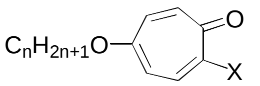
Unsymmetrical bis(5-alkoxy-2-aminotroponato)coppers showed tilted smectic C and G/J phases due to the alignment of the outboard dipole moment. Furthermore, their *N*, *N*-dimethyl derivatives had nematic and smectic A phases with low transition temperatures due to the reduction of the lateral overlapping and the steric repulsion of the methyl groups.

One of the most important characteristics of troponoids is to make complexes with various metal ions.[1] Based on this point, two research groups reported recently preparation and mesomorphic properties of bis(5-alkoxytropolonato)coppers (**1**), which had highly ordered smectic phases with high transition temperatures.[2] These mesomorphic properties were largely depending on the metal ions; copper complexes were mesomorphic whereas zinc ones were not. These results were explained by the coordination structure of complexes. X-ray crystallographic analysis[2a] of bis(5-octyloxytropolonato)copper complex showed an approximately planar molecular structure as has been observed in the copper complex of tropolone[3] while the coordination structure of a zinc complex might be tetrahedral.

Complexes **1**, however, gradually decomposed during differential scanning calorimetry (DSC) measurements or observing photographs of mesophases due to the high transition temperatures. In this paper, we report preparation of bis(5-alkoxy-2-aminotroponato)coppers (**2**) with an unsymmetrical structure to decrease transition temperatures. Furthermore, we introduced alkyl groups on the nitrogen atoms to decrease the molecular packing force.



1: X=O
2: X=NH
6: X=NMe
7: X=NEt



3: X=NH_2
4: X=OMe
5: X=OH

5-Alkoxy-2-aminotropones (**3**) were prepared by the reaction of 5-alkoxy-2-methoxytropones (**4**), which was obtained from the reaction of 5-alkoxytropolones (**5**)[2,4] with diazomethane, and 28% aqueous ammonia in methanol at 100 °C in a sealed tube. Their metal complexes **2**[5] were prepared by the reaction of compounds **3** and copper acetate in refluxing methanol. The transition temperatures and the thermal behavior of the texture were determined using a polarizing microscope equipped with a hot stage, DSC measurements, and X-ray diffraction study. As summarized in Table 1, complexes **2** have the lower transition temperatures than the corresponding **1**. But their DSC indicated the partial decomposition around clearing points.

Table 1. Transition temperatures (°C) of tropolonato (**1**) and aminotroponato (**2**) coppers

	n	C	S_G or S_J	B(cry)	B(hex)	S_C	I
1a	10[a]	● 250			● (248)		●
2a	10	● 138	● 188			● 190	●
1b	12[b]	● 170		● 191	● 237	● 240	●
2b	12	● 135	● 191			● 218	●
1c	14[a]	● 234		(● 183	● 235)	● 236	●
2c	14	● 120	● 190			● 203	●

C: crystals, $S_{G(J)}$: smectic G (J) phase, B(cry): crystal B, B(hex): hexatic B,
S_C: smectic C phase, I: isotropic liquid. [a]Reference 2a. [b]Reference 2b.

Compound **2c** showed schlieren textures around 200 °C and broken mosaic textures around 150 °C. Powder X-ray diffraction studies of compound **2c** showed three sharp peaks at 200 °C corresponding to the (001), (002), and (003) reflections and five ones at 150 °C at the small angle regions to indicate a higher periodicity in a lamellar layered structure. The layer spacings (d) of the mesomorphic phases both at 200 and 150 °C were observed to be 34.9 and 35.3 Å, respectively. Since the calculated molecular length is 50.5 Å by MM2 method, we determined that they are smectic C and smectic G/J phases with tilt angle of 46 ° when alkyl chains are not interdigitated. When compared with their transition temperatures between complexes **1** and **2**, the latter has only the tilted phases with the lower transition temperatures than the former.

Next, we prepared complexes **6**[5] with two methyl groups on the nitrogen atoms in the core part of complexes **2**. Highly ordered smectic phases disappeared to exhibit softer liquid crystalline phases such as nematic and smectic A phases as shown in Table 2. The nematic phase was assigned from the observation of schlieren and droplet textures and the smectic A phase from the focal-conic fan and homeotropic textures. By introducing two methyl groups, the clearing points decreased extremely although their melting points were almost identical to those of compounds **2**. The powder X-ray diffraction study of compound **6b** gave that the layer

Table 2. Transition temperatures (°C) of compounds **6**

	n	C	S_A	N	I
6a	10	● 124	● 130	● 131	●
6b	12	● 121	● 129		●
6c	14	● 121	● 126		●

N: nematic phase.

spacing of the smectic A phase is 39.1 Å whereas the calculated molecular length is 45.7 Å. A molecular packing model (d/l = 0.86) of **6b**, in which alkyl chains are interdigitated, is proposed. When two ethyl groups were introduced into the core, complexes **7** were not mesomorphic because of the bulkiness of the lateral substituents.

Complexes **2** have only tilted phases whereas complexes **1** have both tilted and orthogonal ones. Although the dipole moments of symmetrical complexes **1** have a position at the center of the molecules, those of unsymmetrical **2** direct outboard. These outboard dipole moments become aligned as shown in Figure 1 by tilting the molecules with respect to the layer normal.[6] While two methyl groups were introduced in the core of the tilted molecules, the steric repulsion took place between the lateral methyl groups. There are two molecular alignments to relieve the steric repulsion between the methyl groups. One is an inward molecular shift and the other is an outward one. The former should induce a perpendicular alignment to form smectic A phases and the latter would loose the overlapping between the core parts. While the alkyl chains of complexes **6** are short, nematic phases appeared. This must be explained by the reduction of the lateral overlapping caused by the methyl groups.

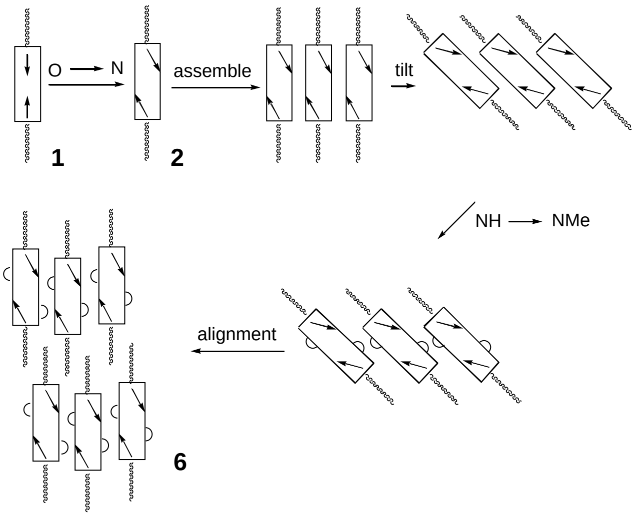


Figure 1. Schematic packing models for troponoid metallomesogens.

In conclusion, we prepared new types of troponoid metallomesogens with two nitrogen atoms in a molecule. By introduction of unsymmetry into molecules, we could reduce transition temperatures. Furthermore, when two methyl groups were introduced on the trivalent nitrogen atoms, nematic and smectic A phases were observed instead of highly ordered smectic phases. These *N*,*N*-dimethyl metallomesogens with lower transition temperatures should be a suitable candidate to measure physical properties such as paramagnetization, electric conductivity, and so on in mesophases.[7]

References and Notes

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5 Elemental analysis: **2a**; brown crystals; Found: C, 66.54; H, 8.64; N, 4.59%. Calcd for $C_{34}H_{52}CuN_2O_4$: C, 66.26; H, 8.50; N, 4.55%. **2b**; brown crystals; Found: C, 67.73; H, 8.94; N, 4.20%. Calcd for $C_{38}H_{60}CuN_2O_4$: C, 67.87; H, 8.99; N, 4.17%. **2c**; brown crystals; Found: C, 69.19; H, 9.41; N, 3.87%. Calcd for $C_{42}H_{68}CuN_2O_4$: C, 69.24; H, 9.41; N, 3.85%. **6a**; yellow crystals; Found: C, 67.39; H, 8.89; N, 4.24%. Calcd for $C_{36}H_{56}CuN_2O_4$: C, 67.10; H, 8.76; N, 4.25%. **6b**; yellow crystals; Found: C, 68.27; H, 9.16; N, 3.99%. Calcd for $C_{40}H_{64}CuN_2O_4$: C, 68.58; H, 9.21; N, 4.00%. **6c**; yellow crystals; Found: C, 69.65; H, 9.40; N, 3.68%. Calcd for $C_{44}H_{72}CuN_2O_4$: C, 69.85; H, 9.59; N, 3.70%.

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