

Bimetallo mesogens: formation of calamitic or columnar mesophases by μ -exogenous-bridged groups in N,N' -(propan-2-ol)-bis(4-alkoxysalicylaldehyde)copper(II) complexes[†]

Shou-Ming Ku, Chin-Yi Wu and Chung K. Lai*

Department of Chemistry, National Central University, Chung-Li, Taiwan, ROC

Received 24th July 2000, Accepted 11th September 2000

First published as an Advance Article on the web 28th September 2000

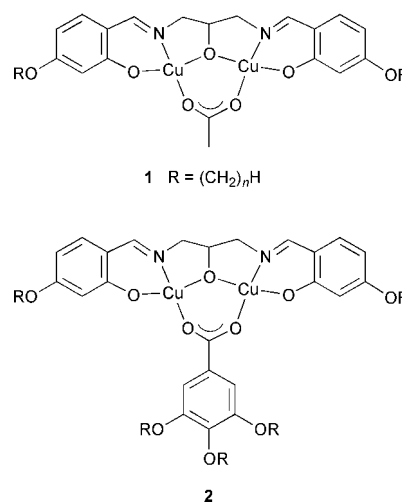
A new type of dicopper(II) complex derived from μ -exogenous 3,4,5-trialkoxybenzoate- or acetate-bridged N,N' -(propan-2-ol)-bis(4-alkoxysalicylaldehydes) prepared by the condensation of 2-hydroxy-4-alkoxybenzaldehydes with 1,3-diaminopropan-2-ol are reported; the formation of mesomorphic phases was found to be dependent upon the bridging groups used, acetate-bridged compounds formed a smectic A (SmA) phase and benzoate-bridged compounds formed a hexagonal columnar (Col_h) phase.

Designing a new type of mesogenic structure which exhibits mesomorphic and physical properties has been a major challenge for materials chemists. A delicate balance between molecular interaction and the precise control of molecular order in extended structures is particularly important for the formation of materials with mesomorphic properties. Recently this approach has been widely applied in the generation of new metallo mesogens¹ derived from transition metal incorporated coordination compounds because of their versatility in molecular geometry and their known rich chemistry. The continuing preparation of new structures and/or geometric shapes provides us with an opportunity to test the boundary in metallo-mesogenic materials.

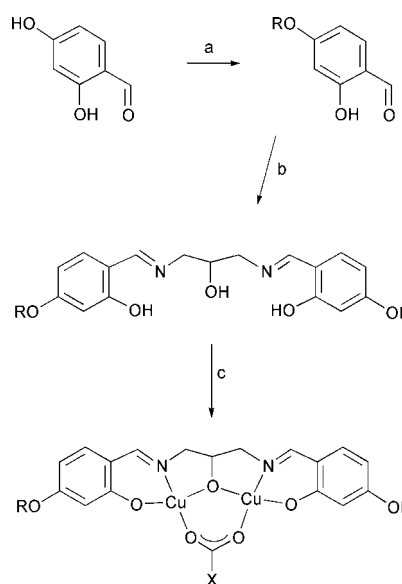
As part of our continuing research² on bimetallo mesogens, in this communication we report our recent results on the preparation and mesomorphic properties of copper complexes derived from N,N' -(propan-2-ol)-bis(4-alkoxysalicylaldehydes). This new type of Schiff-base derivative is structurally catalogued as a pentadentate ligand and is capable of forming binuclear complexes with exogenous- or endogenous-bridging groups. Acetate or 3,4,5-trialkoxybenzoate ion was used in this work as the μ -exogenous-bridging group due to its preferred two-atom planar bonding. These prepared copper complexes were found to exhibit enantiotropic smectic or columnar phases depending on the bridging group used. Acetate-bridged compounds **1** formed a smectic A (SmA) phase, whereas 3,4,5-trialkoxybenzoate-bridged compounds **2** formed a hexagonal columnar (Col_h) phase.

The synthetic procedures for copper complexes **1** and **2** is summarized in Scheme 1. The aldimine Schiff-base derivatives were obtained as light yellow crystals formed by condensation of two equivalents of 2-hydroxy-4-alkoxybenzaldehyde with one equivalent of 1,3-diaminopropan-2-ol in refluxing ethanol with yields in the range 78–92%.[†] ¹H-NMR spectroscopic data showed one characteristic peak at 8.20 ppm assigned to imine-H (–N=CH). The reactions of these Schiff bases with copper acetate monohydrate in refluxing ethanol produced the title copper complexes. Recrystallization from methylene chloride–methanol gave light blue needle crystals. These dicopper compounds are all paramagnetic, and the ¹H- and ¹³C-NMR (Bruker DRS-200, 200 MHz) display only broad alkoxy signals. Elemental analysis of these complexes was also performed.[†]

The liquid crystalline behavior of these copper complexes



was studied by thermal analysis (DSC) and polarizing optical microscopy. The phase transitions and thermodynamic data for complexes **1** and **2** are summarized in Table 1. All the copper complexes exhibited enantiotropic behavior. Acetate-bridged compounds **1** were found to form a smectic phase. Transitions of crystal-to-mesophase for the complexes were observed from 143.2–171.6 °C on heating with transition enthalpies 9.10–15.74 kJ mol^{–1} and the clearing points were in the range of 159.4–177.4 °C. All the melting and clearing temperatures slightly



Scheme 1 Reagents and conditions: (a) RBr (1.1 eq, R = (CH₂)_nH), KHCO₃ (1.0 eq), K₁ (cat.), refluxing in CH₃COCH₃, 24 h. 70–83%. (b) H₂NCH₂CH(OH)CH₂NH₂ (0.5 eq), refluxing in absolute C₂H₅OH, 5 h. 80–92%. (c) X = CH₃, Cu(OAc)₂ (2.2 eq), refluxing in absolute C₂H₅OH, 24 h. 72–87%, X = C₆H₂(OR')₃ (1.1 eq), Cu(NO₃)₂ (2.2 eq), KOH (1.1 eq), refluxing in dried THF/MeOH, 18 h. 62–85%.

[†]Electronic supplementary information (ESI) available: elemental analysis data for compounds **1** and **2**. See <http://www.rsc.org/suppdata/dt/b0/b005936f>

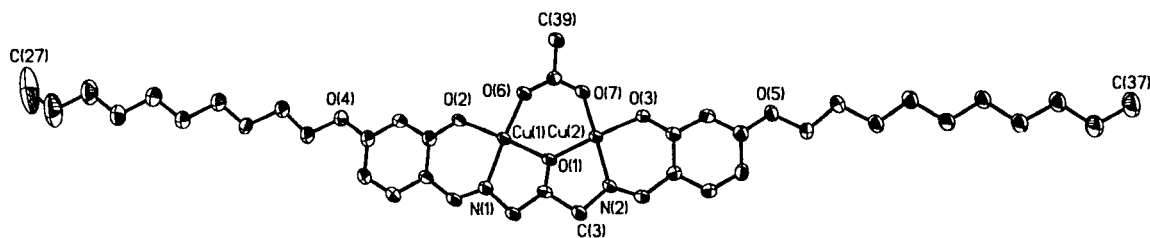


Fig. 1 ORTEP⁶ drawing for copper(II) complex **1** ($n = 10$) with the atomic numbering scheme. Thermal ellipsoids drawn at the 50% probability level.

Table 1 Phase behavior^a of copper complexes **1** and **2**

1 $n = 10$	K	$\frac{171.6 (11.9)}{115.1 (0.35)}$	SmA	$\frac{177.4 (3.51)}{169.7 (2.81)}$	I
		$\frac{167.7 (15.2)}{114.9 (0.78)}$		$\frac{175.7 (3.82)}{171.4 (3.83)}$	
	12 K	$\frac{160.0 (15.7)}{111.3 (0.59)}$	SmA	$\frac{172.0 (3.40)}{166.6 (4.44)}$	I
		$\frac{151.5 (11.7)}{106.7 (0.29)}$		$\frac{164.4 (2.52)}{159.2 (2.45)}$	
2 $n = 10$	14 K	$\frac{143.2 (9.10)}{106.4 (0.79)}$	SmA	$\frac{159.4 (3.33)}{155.6 (2.93)}$	I
		$\frac{61.1 (1.28)}{59.3 (1.25)}$		$\frac{146.5 (5.30)}{138.0 (6.49)}$	
	14 K	$\frac{53.4 (19.7)}{38.1 (19.6)}$	Col _h	$\frac{145.9 (9.36)}{140.8 (9.32)}$	I
		$\frac{63.6 (29.8)}{44.8 (30.7)}$		$\frac{144.7 (9.13)}{138.5 (9.31)}$	

^a n = No. of carbons in the sidechain; K = crystal phase; SmA = smectic A phase; Col_h = columnar hexagonal phase; I = Isotropic. The transition temperature (°C) and enthalpies (in parentheses, kJ mol⁻¹) are determined by DSC at a scan rate of 10.0 °C min⁻¹.

decreased with increasing length of the alkoxy sidechains, however, the temperature range of the mesophase remained at *ca.* 49.0–56.0 °C on cooling. The mesophase was characteristically identified as smectic A (SmA) based on the observed optical texture.⁴ A typical fan texture was clearly observed on slowly cooling from the isotropic liquid, which is often obtained for rod-like molecules. This smectic A phase was also established by observation of a homeotropic texture without subjecting the sample to mechanical stress. However, all compounds **2** with 3,4,5-trialkoxybenzoate as the bridging group exhibited a hexagonal columnar (Col_h) phase. All compounds **2** gave two typical transitions of crystal-to-columnar and columnar-to-isotropic (K→Col→I) by DSC analysis. A relatively larger enthalpy for the columnar-to-isotropic transition was observed at higher temperatures (144.7–146.5 °C) indicating that the mesophases were highly ordered. When cooled from their isotropic phase, they displayed an optical texture which was a mixture of pseudo focal-conics and mosaic regions with linear birefringent defects, suggesting hexagonal columnar structures.

Single-crystal X-ray structural analysis⁵ was performed at 150 K for copper complex **1** ($n = 10$). The blue needle crystal was obtained at a CH₂Cl₂–CH₃OH (1/1) interface at room temperature. Fig. 1 shows the molecular structure with the atomic numbering scheme. The aldimine Schiff base derivative is binucleating and the two copper(II) ions are bridged by the secondary alkoxo and the acetate moiety. The compound contained two uncoordinated molecules of methylene chloride in the crystal lattice. There are no significant intermolecular interactions between neighboring binuclear entities. The overall molecular shape is rod-like and nearly flat, and the intramolecular Cu...Cu distance is 3.498 Å. Both copper(II) centers have essentially planar coordination of the N₂O₂ donor sets and the two copper atoms are in *cis* position, 0.044 and 0.056 Å off the core planes defined by atoms of O1, O3, O7 and N2, and O1, N1, O2 and O6, respectively. The two angles O(2)–Cu(1)–N(1) and O(2)–Cu(1)–O(6) are 93.8(2) and 87.2(2)°, which show a small deviation from the ideal angle of 90° expected for a square-planar complex. The overall length (from C27 to C37) and the width (from C39 to C3) of the molecule are 41.50 and 6.82 Å, respectively.

Bimetalloesogenic structures exhibiting columnar or smectic phases were generated and characterised by using acetate or benzoate bridging groups.

This work was supported by the National Science Council of Taiwan, ROC under grant NSC-89-2113-M-008-008.

Notes and references

‡ 2-Hydroxy-4-dodecanoxybenzaldehyde. Yield 67%, white crystals. ¹H-NMR (ppm, CDCl₃): 0.86(t, –CH₃, 3H), 1.06–1.80(m, –CH₂, 20H), 3.98(t, –OCH₂, 2H), 6.38(d, –C₆H₃, 1H), 6.52(dd, –C₆H₃, 1H), 7.39(d, –C₆H₃, 1H), 9.68(s, –CHO, 1H), 11.4(s, –OH, 1H). ¹³C NMR (ppm, CDCl₃): 14.17, 22.65, 25.87, 28.91, 29, 29.13, 29.46, 29.55, 29.72, 31.91, 68.6, 100.9, 108.8, 114.9, 135.0, 164.4, 166.4, 194.2.

N,N'-(Propan-2-ol)-bis(4-dodecanoxysalicylaldimine). A solution of 2-hydroxy-4-dodecanoxybenzaldehyde (3.00 g, 0.01 mol) dissolved in hot absolute ethanol (75 ml) was slowly added to 1,3-diaminopropan-2-ol (0.45 g, 5.0 mmol). The mixture was refluxed for 3 h. A yellow solid was obtained upon cooling at room temperature. The crude solids were collected and recrystallized from methylene chloride to give light yellow crystals. Yield 85%. ¹H-NMR (ppm, CDCl₃): 0.85(t, –CH₃, 6H), 1.15–1.74(m, –CH₂, 40H), 3.54–3.78(m, –NCH₂, 4H), 3.93(t, –OCH₂, 4H), 4.17(t, –CH, 1H), 6.34(d, –C₆H₃, 2H), 6.42(s, –C₆H₃, 2H), 7.08(d, –C₆H₃, 2H), 8.20(s, –N=CH, 2H). ¹³C NMR (ppm, CDCl₃): 13.98, 22.54, 25.85, 28.93, 29.20, 29.25, 29.43, 29.46, 29.49, 29.52, 31.76, 60.85, 67.95, 70.03, 100.85, 101.62, 106.92, 111.65, 132.92, 163.68, 165.70. IR (thin film): 1023, 1111, 1214, 1322, 1372, 1524, 1632, 2827, 2909, 3424 cm⁻¹.

N,N'-(Propan-2-ol)-bis(4-dodecanoxysalicylaldimino)copper(II) **1**, $n = 12$. A hot ethanol (25.0 ml) solution of *N,N'*-(propan-2-ol)-bis(4-dodecanoxysalicylaldimine) (0.30 g, 0.45 mmol) was added to a hot methanol solution of copper(II) acetate monohydrate (0.20 g, 1.0 mmol). The solution intermediately turned blue-greenish in color and the solution was held at a gentle reflux for 24 h. The solution was then concentrated to give a blue solid. Recrystallization from CH₂Cl₂–MeOH gave blue needle crystals. Yield 80%. IR (thin film): 1023, 1063, 1144, 1171, 1231, 1312, 1426, 1524, 1610, 2848, 2923 cm⁻¹. Anal. Calcd. for C₄₁H₆₃N₂O₅Cu₂: C 60.68, H 7.94. Found C 59.92, H 7.70%.

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- Crystal data for **1** ($n = 10$): C₄₃H₆₇Cl₄Cu₂N₂O₂, $M = 963.81$, triclinic, space group $P\bar{1}$, $a = 10.1239(1)$, $b = 11.1114(1)$, $c = 20.6214(3)$ Å, $\alpha = 84.247(1)$, $\beta = 85.490(1)$, $\gamma = 80.884(1)^\circ$, $V = 2274.23(4)$ Å³, $Z = 2$, $D_c = 1.407$ Mg m⁻³, $T = 150(1)$ K, final R indices $R1 = 0.0828$, $wR2 = 0.2203$, crystal size $0.40 \times 0.16 \times 0.16$ mm. Siemens SMART CCD diffractometer, 7868 independent reflections and 23989 reflections collected. The structure was solved by direct methods. Hydrogen atoms were fixed at calculated positions and refined using a riding model. CCDC reference number 186/2182. See <http://www.rsc.org/suppdata/dt/b0/b005936f/> for crystallographic files in .cif format.
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