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Steric effect on the formation of columnar phases in β -diketonate copper(II) complexes

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A systematic study of the mesomorphic properties of three series of copper(II) complexes based on β -diketonate ligands containing branched side chains is reported. These disc-like compounds have four, six and eight flexible alkoxy side chains appended to the central core, in which two or four side chains were substituted by bulkier secondary alkoxy groups: 1-methylbutyloxy $R' = C_5(2^\circ)$ or 1-methylheptyloxy $R' = C_8(2^\circ)$. The mesomorphic results indicated that at least eight side chains are required to form stable columnar mesophases; other compounds with four or six side chains are not mesogenic regardless of the combination of the carbon length on the alkoxy or secondary alkoxy groups of the side chains. The compounds **3** with shorter $R' = C_5(2^\circ)$ side chains were all non-mesogenic regardless of the carbon length of three alkoxy side chains ($R = C_8, C_{10}, C_{12}$) used. However, when the longer 1-methylheptyloxy side chain $R' = C_8(2^\circ)$ was substituted, the compounds **3b–3e** with various alkoxy groups ($R = C_6, C_7, C_8, C_{10}, C_{12}$) exhibited columnar phases. The mesophases were characterized and identified as columnar hexagonal phases (Col_h), as expected, by thermal analysis and optical polarized microscopy. The presence of the introduced secondary alkoxy groups apparently appeared to influence the formation of columnar phases. The clearing points were relatively lower than other similar copper(II) compounds not substituted by secondary alkoxy side chains.

1. Introduction

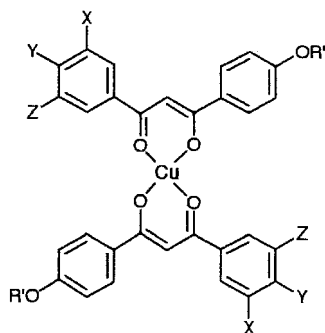
The formation of columnar mesophases [1] is often accomplished by molecules with a variety of overall molecular shapes, such as disc-like, half-disc or possibly rod-like molecules. In this phase the central core is stacked to form columns surrounded by numerous disordered flexible side chains. The organization of antiparallel correlation, as a result of dipolar forces, by half-disc or rod-like molecules to form columnar phases is also feasible, particularly in metallomesogenic structures due to intermolecular coordinative forces. In general the stability of the columnar mesophases formed by these molecules is determined and/or controlled by the number of flexible side chains (i.e. side chain density) attached to the central core. On the other hand more flexible side chains or longer carbon length of side chains are fre-

quently needed to stabilize a larger central core. Among many metallomesogenic structures bis(β -diketonate)-metal(II) complexes [2–6] are the ones most studied. Various mesophases [1] exhibited by these metal complexes are known: discotic lamellar (D_L), columnar hexagonal (Col_h), columnar rectangular (Col_r) and nematic (N) phases. Studies of mesomorphic properties indicated that in this particular metallomesogenic structure six or more flexible alkoxy side chains are found to be required for the formation of stable columnar phases. The introduction of chiral side chains in metallomesogenic structures to generate tilted columnar mesophases [7, 8] with a helical structure has also been studied recently.

In order to understand the effect of steric substituent groups attached to the phenyl ring of β -diketones on the formation of columnar phases, we systematically prepared three series of copper(II) β -diketonate complexes **1–3**. These compounds have four, six and eight alkoxy side chains, respectively. In series **1** and **3**, two

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flexible side chains were substituted by secondary alkoxy groups: 1-methylbutyloxy $C_5(2^\circ)$ or 1-methylheptyloxy $C_8(2^\circ)$. In series **2** four side chains were similarly substituted.



- 1** Y = OR; X = Z = H
1a R' = $C_5(2^\circ)$, R = C_{10}
1b R' = $C_8(2^\circ)$, R = C_{10}
2 X = Z = OR; Y = H
2a R' = $C_8(2^\circ)$, R = C_{12}
2b R' = $C_8(2^\circ)$, R = C_{16}
2c R' = C_{16} , R = $C_5(2^\circ)$
2d R' = C_{16} , R = $C_8(2^\circ)$
3 X = Y = Z = OR
3a R' = $C_5(2^\circ)$, R = C_{12}
3b R' = $C_8(2^\circ)$, R = C_6
3c R' = $C_8(2^\circ)$, R = C_7
3d R' = $C_8(2^\circ)$, R = C_8
3e R' = $C_8(2^\circ)$, R = C_{12}
3f R' = $C_8(2^\circ)$, R = C_{14}

2. Results and discussion

2.1. Synthesis and characterization

The compounds 4-(1-methylbutyloxy)acetophenone and 3,5-di(1-methylheptyloxy)acetophenone were prepared by analogous methods by Mitsunobu reactions [9, 10]. They were obtained by the reaction of 4-hydroxyacetophenone or 3,5-dihydroxyacetophenone with 2-pentanol or 2-octanol in the presence of triphenyl phosphine (TPP) and diisopropyl azodicarboxylate (DIAD) in dried THF at room temperature. These secondary ether ketones were isolated as light yellow oils in yields of 70–83%. The β -diketonate ligands were prepared by Claisen condensation of the appropriate methyl benzoate ester and the acetophenone in the presence of sodium hydride. The products were separated and purified by flash column chromatography, eluting with a mixture of ethyl acetate/*n*-hexane (v/v 1/19). These compounds were obtained as viscous dark yellow to orange pastes; yields were 67–87%. All these organic compounds were characterized by ^1H and ^{13}C NMR spectroscopy.

The reaction of β -diketonate ligands with $\text{Cu}(\text{OAc})_2$ produced the copper(II) complexes in yields of 72–85%. These copper(II) complexes were obtained as light green solids or green pastes depending on the carbon length of the side chains. The solid complexes were purified by recrystallization from $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$ (v/v 1/1); the

oily paste complexes were separated by flash column chromatography, eluting with a mixture of ethyl acetate/*n*-hexane (v/v 1/9). These complexes were characterized by IR spectroscopy and elemental analysis. Satisfactory elemental analyses for all compounds were obtained, see table 1.

2.2. Mesomorphic properties of compounds **1** and **2**

All known metal β -diketonate complexes ($M = \text{Cu}, \text{Pd}, \text{VO}$) appended with four symmetric or unsymmetrical alkoxy side chains, are reported to be non-mesogenic [1]. The lack of liquid crystallinity is attributed to strong intermolecular forces between the neighbouring molecules in the columns, and the mesomorphic properties are often improved by increasing the numbers of flexible side chains (i.e. side chains density) attached to the central core. The numbers of the side chains were increased to, for example, six, eight, ten or twelve, and all reported compounds with eight, ten or twelve side chains exhibited better mesomorphic properties. Our initial thought was to increase the side chain steric hindrance, in hope that the bulkiness of substituent groups might weaken the intermolecular attraction. Therefore, three series of copper(II) complexes based on unsymmetrical β -diketonate ligands have been prepared. In these compounds a systematic combination of various carbon length chains on either side of the two phenyl rings was applied to alter the steric bulkiness of the whole molecules. In compounds **1** and **2**, in two or four side chains were substituted by bulkier secondary 1-methylbutyloxy [$C_5(2^\circ)$] or 1-methylheptyloxy [$C_8(2^\circ)$] groups. The mesomorphic properties for all the copper complexes was studied by thermal analysis (DSC) and polarizing microscopy. The phase behaviour for copper complexes **1** and **2** are summarized in table 2. All the compounds exhibited crystalline phases regardless of the combination of the carbon length of alkoxy side chains ($R = C_{10}, C_{12}, C_{16}$) or secondary side chains [$R' = C_5(2^\circ)$]

Table 1. Elemental analysis of complexes **1**–**3** with calculated values in parentheses

Compds	C/%	H/%
1a	72.28 (72.44)	8.24 (8.31)
1b	73.44 (73.47)	8.86 (8.78)
2a	74.62 (75.08)	9.74 (10.05)
2b	76.49 (76.45)	10.36 (10.61)
2c	73.83 (73.75)	9.60 (9.51)
2d	74.58 (75.08)	9.97 (10.53)
3a	75.45 (75.23)	10.29 (10.48)
3b	71.82 (72.02)	9.48 (9.28)
3c	72.56 (72.81)	9.81 (9.58)
3d	73.48 (73.52)	9.86 (9.84)
3e	75.82 (75.70)	10.67 (10.66)
3f	76.45 (76.51)	10.80 (10.96)

Table 2. Phase behaviour of the compounds **1–3**. K = crystal phase; Col_{hd} = columnar disordered hexagonal phase; I = isotropic. The transition temperature (°C) and enthalpies (in parenthesis, kJ/mol) are determined by DSC at a scan rate of 10.0°C/min.

1a	Cr	$\xrightarrow[124.5 (44.0)]{154.6 (57.9)}$	I
1b	Cr	$\xrightarrow[115.0 (32.1)]{133.5 (36.0)}$	I
2a	Cr	$\xrightarrow[55.5 (45.5)]{90.3 (54.3)}$	I
2b	Cr	$\xrightarrow[55.2 (51.1)]{83.2 (51.7)}$	I
2c	Cr	$\xrightarrow[< 20.0]{83.5 (20.8)}$	I
2d	Cr	$\xrightarrow[< 20.0]{62.6 (73.8)}$	I
3a	Cr	$\xrightarrow[32.0^a]{67.0 (131)}$	I
3b	Cr	$\xrightarrow[73.1 (24.6)]{82.2 (4.13)}$	Col _{hd}
	Col _{hd}	$\xrightarrow[32.6 (0.76)^a]{82.2 (4.13)}$	I
3c	Cr	$\xrightarrow[33.5^a]{78.1^a}$	Col _{hd}
	Col _{hd}	$\xrightarrow[50.0^a]{78.1^a}$	I
3d	Cr	$\xrightarrow[48.5 (1.56)]{68.3 (74.5)}$	Col _{hd}
	Col _{hd}	$\xrightarrow[53.0^a]{68.3 (74.5)}$	I
3e	Cr	$\xrightarrow[62.9 (111)]{68.3 (2.78)}$	Col _{hd}
	Col _{hd}	$\xrightarrow[< 20.0]{68.3 (2.78)}$	I
3f	Cr	$\xrightarrow[30.2 (55.6)]{69.2 (67.1)}$	I

^a Values observed by microscopy.

or C₈(2°)] used. Crystal-to-isotropic transitions were all observed. The clearing points were all apparently lower than those reported for complexes without secondary side chains.

2.3. Mesomorphic properties of compounds **3**

When side chain numbers were increased to eight, the mesomorphic properties was greatly improved. Complexes **3b–3e** exhibited columnar phases and the compounds **3b** and **3f** formed crystalline phases. Compounds **3** with secondary 1-methylbutyloxy side chains $R' = C_5(2^\circ)$ were all non-mesogenic regardless of the carbon length of three alkoxy side chains ($R = C_8, C_{10}, C_{12}$) used. However when secondary 1-methylheptyloxy side chains $R' = C_8(2^\circ)$ were used compounds **3b–3e** exhibited columnar phases ($R = C_6, C_7, C_8, C_{10}, C_{12}$). These compounds melt to give a birefringent fluid phase with an optical texture of pseudo focal-conics, with linear birefringent defects and large areas of uniform homeotropic domains, typically of hexagonal columnar discotic structures. In contrast to columnar rectangular phases,

mosaic textures with wedge-shaped defects were often observed. In DSC analysis, compounds **3c** and **3d** formed monotropic phases, and **3b** and **3e** formed enantiotropic phases. DSC showed a larger enthalpy for the crystal-to-liquid crystal transition at lower temperature and a relatively lower enthalpy for the liquid crystal-to-isotropic transition at higher temperature, indicating the mesophase to be in highly disordered state. The temperature range of mesomorphism is narrow. The identification of columnar hexagonal columnar phases was characterized by optical textures, and confirmed by variable-temperature X-ray powder diffraction (XRD).

The results showed that recurrence of liquid crystallinity depended not only on the numbers and type of side chains but also on the distribution of electron polarization. As a result, four or six side chains does not contribute enough electron density for β -diketonate cores to form stable discotic mesophases. Dipole interaction between cores is relatively weak.

3. Summary and conclusion

Copper(II) β -diketonate complexes with a combination of various numbers and/or secondary [$R' = C_5(2^\circ)$ or $C_8(2^\circ)$] substitution of alkoxy side chains were prepared. Their mesomorphic properties were investigated, to understand the steric effect of substitution on the formation of columnar phases. We have found that the numbers of side chains played an important role in controlling the core–core interactions which determined the formation of the liquid crystallinity. In addition, the degree of polarization distribution of side chain density, by choosing steric secondary side chains, apparently influenced the formation and stability of the mesophases. Although eight side chains are required to form stable mesophases, the introduction of more steric secondary side chains reduced the core–core interaction and lowered the clearing points.

4. Experimental

All chemicals and solvents were reagent grades (Aldrich Chemical Co.) and used without further purification. THF and dimethoxyethane (DME) were dried over sodium benzophenone ketyl. ¹H and ¹³C NMR spectra were measured on a Bruker AC-300F instrument. Infrared spectra were recorded on a Nicolet Magna II 550 spectrometer using polystyrene as standard. DSC thermographs were carried out on a Perkin-Elmer DSC-7. All phase behaviours were determined at a scan rate of 10°C min⁻¹. Optical polarized microscopy was carried out on a Nikon Microphot-FXA with a Mettler FP90/FP82HT hot stage system. XRD studies were conducted on an Inel MPD-diffractometer with a 2 kW CuK α X-ray source equipped with an INEL CPS-120 position sensitive detector.

4.1. 4-(1-Methylbutyloxy)acetophenone

4-Hydroxyacetophenone (5.0 g, 36.7 mmol), 2-pentanol (3.24 g, 36.7 mmol) and triphenyl phosphine (12.0 g, 0.046 mol) were mixed and dissolved in 175 ml of dried THF. To this solution was added dropwise diisopropyl azodicarboxylate (DIAD, 9.30 g, 0.046 mol) dissolved in 25 ml of THF at 0°C. The reaction mixture was stirred at room temperature for 2 days. Water (*c.* 5 drops) was added to the solution, and the mixture stirred for 1 h. The solution was concentrated to give a yellow liquid and white solids. The solids were filtered off, and the yellow liquid was purified by flash chromatography with an eluant of ethyl acetate/hexane (1/10). Yield 83%, light yellow oil. ¹H NMR (ppm, CDCl₃): 0.86 (t, -CH₃, 3H), 1.30 (d, CH₃CHO, 3H), 1.31–1.77 (m, -CH₂, 4H), 2.55 (s, COCH₃, 3H), 4.46 (m, -OCH, 1H), 6.91 (d, -C₆H₄, 2H), 7.91 (d, -C₆H₄, 2H). ¹³C NMR (ppm, CDCl₃): 13.63, 18.31, 19.19, 38.10, 25.82, 73.34, 114.7, 129.5, 130.3, 162.0, 196.1. IR (neat): 2961, 2874, 1677, 1600, 1507, 1254, 1111 cm⁻¹.

4.2. 4-(1-Methylheptyloxy)acetophenone

Yield 79%, light yellow oil. ¹H NMR (ppm, CDCl₃): 0.79 (t, -CH₃, 3H), 1.22 (d, CH₃CHO, 3H), 1.29–1.69 (m, -CH₂, 4H), 2.43 (s, COCH₃, 3H), 4.34 (m, -OCH, 1H), 6.80 (d, -C₆H₄, 2H), 7.81 (d, -C₆H₄, 2H). ¹³C NMR (ppm, CDCl₃): 13.79, 19.31, 22.32, 25.15, 28.96, 31.50, 36.06, 25.93, 73.72, 114.8, 129.6, 130.3, 162.1, 196.2. IR (neat): 2961, 2874, 1677, 1600, 1507, 1254, 1111 cm⁻¹.

4.3. 3,5-Di(1-methylheptyloxy)acetophenone

Yield 78%, light yellow oil. ¹H NMR (ppm, CDCl₃): 0.85 (t, -CH₃, 3H), 1.27 (d, CH₃CHO, 3H), 1.35–1.73 (m, -CH₂, 20H), 2.53 (s, COCH₃, 3H), 4.36 (q, -OCH₂, 2H), 6.58 (t, -ph, 1H), 7.01 (d, -ph, 2H). ¹³C NMR (ppm, CDCl₃): 13.75, 15.81, 23.71, 27.05, 27.27, 29.87, 30.05, 32.40, 73.73, 113.51, 115.75, 129.68, 129.65, 130.67, 163.87, 196.44 (C=O). IR (neat): 2960.7, 2873.6, 1678.4, 1600.1, 1507.2, 1254.4, 1110.8 cm⁻¹.

4.4. 1-(4-Decyloxyphenyl)-3-(4-methylbutyloxyphenyl)-propane 1,3-dione

4-(1-Methylbutyloxy)acetophenone (5.0 g, 0.024 mol) and methyl, 4-decyloxybenzoate (6.70 g, 0.024 mol) were mixed in 150 ml of dried THF. The solution was slowly added to NaH (1.75 g, 0.073 mol) suspended in 30 ml of THF, and the reaction mixture was gently refluxed for 24 h. A few drops of 95% ethanol was added to quench the excess NaH, and the solution was neutralized with dilute hydrochloric acid. The solution was extracted

twice with chloroform, and the organic layers were combined and dried over MgSO₄. The solution was concentrated to give a dark brown paste. The product was obtained as an orange paste by flash chromatography with an eluant of ethyl acetate/hexane (1/20). Yield 81%. ¹H NMR (ppm, CDCl₃): 0.89 (m, -CH₃, 6H), 1.26–1.81 (m, -CH₂, 23H), 4.00 (t, -OCH₂, 6H), 4.45 (m, -OCH, 1H), 6.70 (s, HC=CH, 1H), 6.92 (m, -C₆H₄, 4H), 7.90 (m, -C₆H₄, 4H). ¹³C NMR (ppm, CDCl₃): 13.98, 14.08, 18.67, 19.59, 22.64, 25.96, 29.10, 29.29, 29.52, 31.86, 38.45, 68.21, 73.75, 91.30, 114.4, 115.3, 127.7, 128.0, 129.0, 129.1, 131.4, 161.8, 162.6, 184.5. IR (neat): 2964, 2872, 1605, 1460, 1255, 1117 cm⁻¹.

4.5. 1-(3,5-Didodecyloxyphenyl)-3-(4-methylheptyloxyphenyl)-propane 1,3-dione

Yield 85%, orange oily paste. ¹H NMR (ppm, CDCl₃): 0.86 (m, -CH₃, 9H), 1.25–1.81 (m, -CH₂, 53H), 3.98 (t, -OCH₂, 4H), 4.40–4.49 (m, -OCH, 1H), 6.60 (s, -ph, 1H), 6.71 (s, HC=CH, 1H), 6.92 (d, -ph, 2H), 7.06 (s, -ph, 2H), 7.92 (d, -ph, 2H). ¹³C NMR (ppm, CDCl₃): 14.09, 19.61, 22.57, 22.67, 25.42, 26.02, 29.22, 29.35, 29.61, 31.75, 31.90, 36.31, 68.31, 74.09, 92.49, 105.11, 105.36, 115.35, 127.50, 129.31, 137.62, 160.38, 162.09, 184.31, 185.67. IR (neat): 2924.1, 2853.6, 1604.0, 1463.4, 1255.2, 1116.9 cm⁻¹.

4.6. 1-[3,5-Di(methylheptyloxyphenyl)]-3-(4-hexadecyloxyphenyl)-propane 1,3-dione

Yield 78%, orange oily paste. ¹H NMR (ppm, CDCl₃): 0.88 (m, -CH₃, 9H), 1.26–1.81 (m, -CH₂, 54H), 3.99 (t, -OCH₂, 2H), 4.38–4.44 (m, -OCH, 2H), 6.59 (s, -ph, 1H), 6.73 (s, HC=CH, 1H), 6.93 (d, -ph, 2H), 7.06 (s, -ph, 2H), 7.93 (d, -ph, 2H). ¹³C NMR (ppm, CDCl₃): 14.04, 19.68, 22.58, 22.66, 25.48, 25.97, 29.10, 29.27, 29.35, 29.66, 31.78, 31.91, 36.45, 68.20, 74.09, 92.38, 106.55, 107.40, 114.36, 127.76, 129.18, 137.68, 159.51, 162.84, 184.38, 185.55.

4.7. 1-(3,4,5-Trihexyloxyphenyl)-3-(4-methylheptyloxyphenyl)propane 1,3-dione

Yield 83%, orange oily paste. ¹H NMR (ppm, CDCl₃): 0.88 (m, -CH₃, 12H), 1.25–1.84 (m, -CH₂, 37H), 3.95–4.06 (m, -OCH₂, 6H), 4.41–4.49 (m, -OCH, 1H), 6.65 (s, HC=CH, 1H), 6.92 (d, -ph, 2H), 7.16 (s, -ph, 2H), 7.91 (d, -ph, 2H). ¹³C NMR (ppm, CDCl₃): 14.04, 19.63, 22.61, 25.43, 25.78, 29.21, 29.32, 30.27, 31.56, 31.74, 36.32, 69.38, 73.58, 74.11, 91.91, 105.91, 115.17, 127.47, 129.18, 130.66, 142.15, 152.92, 161.99, 184.75, 18491. IR (neat): 2927.3, 2855.9, 1602.9 (C=O), 1491.4, 1466.0, 1254.0, 1115.4 cm⁻¹.

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