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Smectic bimetallomesogens in β-enaminoketonate copper complexes: the steric effect of a methyl substituent on the core group and the crystal structure

Chung K. Lai,* Raymond Lin, Min-Yi Lu and Kwo-Cheng Kao

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

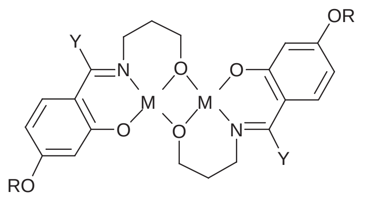
A systematic study has been made of the liquid crystalline properties of two types of copper complexes derived from enamino-β-ketonate and iminopropyl-β-ketonate Schiff bases that exhibit mesomorphism. These complexes are structurally similar, and all have a bimetallic center as an expanded core group. The mesophase stability depends upon the steric bulk between the layer structures. The enamino-β-ketonate complexes exhibit smectic A phases, however, the iminopropyl-β-diketonates are not liquid crystalline. Examination of the structural features of these complexes revealed that the presence of a methyl group attached to the core group was the cause for the lack of liquid crystallinity observed in the latter. The crystal and molecular structure of bis[3,5-dioctanoylphenyl 2-(3-hydroxypropyl)iminopropyl ketonato]copper(II) was determined by means of X-ray analysis. The $\text{Cu}\cdots\text{Cu}$ intramolecular separation is 3.0375(5) Å. The planar geometry is slightly distorted toward square pyramidal by displacement of the copper by 0.018 Å from the mean plane through atoms N(1), O(2), O(1A) and O(1).

While the understanding of structure–property relationships has been progressive, certain guiding principles based on molecular shapes are extensively applied in the design of metallomesogenic materials.[1] The specific type of mesophase formed is strongly dependent on the molecular shape or geometry. Rod-like molecules generally assemble into smectic (S) or nematic (N) phases whereas disc-like molecules tend to exhibit columnar phases.

The induction and the formation of mesophases are mainly controlled and/or determined by attractive interactions between neighboring molecules. These weak attractions are of various types;[2] for example, dipole–dipole, dispersion, hydrogen bonding, charge transfer and dative co-ordination. The magnitude of the molecular interactions is extremely critical in the formation of mesophases: when they are too weak or too strong the liquid crystalline behavior is totally lost. Hence it is fundamentally important to achieve a delicate balance in the magnitude of the molecular interactions by tuning the molecular structures or geometries in order to optimize the thermotropic behavior. Many mesogenic materials with unique molecular shapes and/or novel properties were generated by simply applying such molecular architecture. On the other hand any steric group or substituent connected to the central core often resulted in a sterically unfavorable arrangement,[3] which would completely destroy the mesomorphic properties. Besides, the metal centers incorporated in metallomesogenic structures also play an important role. The co-ordination geometry of the metal center or centers in this type of material greatly influences the molecular packing in the formation of mesophases.

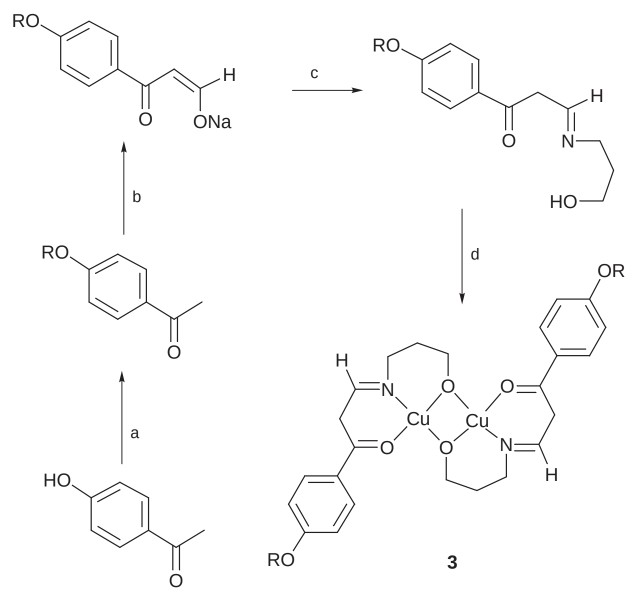
The loss of mesomorphism due to the steric hindrance caused by the presence of an alkyl group has been observed in many mesogenic systems.[4] Metal complexes derived from salicylideneamine and β-diketonate derivatives are among the best known classes of metallomesogens. In these systems the steric hindrance of a tetrahedral methyl group was found to influence the mesomorphism of the molecules. However, the lack of liquid crystallinity due to the methyl group could easily be improved by either use of more elongated terminal groups along the molecular axis or replacement of this methyl group by an H atom with less hindrance. These studies of mesomorphic properties in structurally similar complexes allowed a better understanding of the relationship between structure and properties.

In a previous study we investigated the mesomorphic properties of analogous bis[4-alkoxy-*N*-(3-hydroxypropyl)salicylaldiminato]-copper **1** and -vanadyl complexes[5] **2**, and bis[3,5-bis-(3,4,5-trialkoxybenzyloxy)phenyl 2-(3-hydroxypropyl)iminopropyl ketonato]copper complexes.[6] These complexes are derived from salicylaldimine and β-diketone Schiff bases, and all have a bimetallic structure with oxygen bridging. Studies of the mesomorphic properties concluded that complexes of all ketonate derivatives were non-mesogenic. The bulky tetrahedral methyl group attached to the central core was believed to cause steric disorder in the molecular arrangement, and its steric bulk greatly increased the intermolecular layer distance. This resulted in weakening of the already weak interaction, and therefore destroyed the mesomorphism.

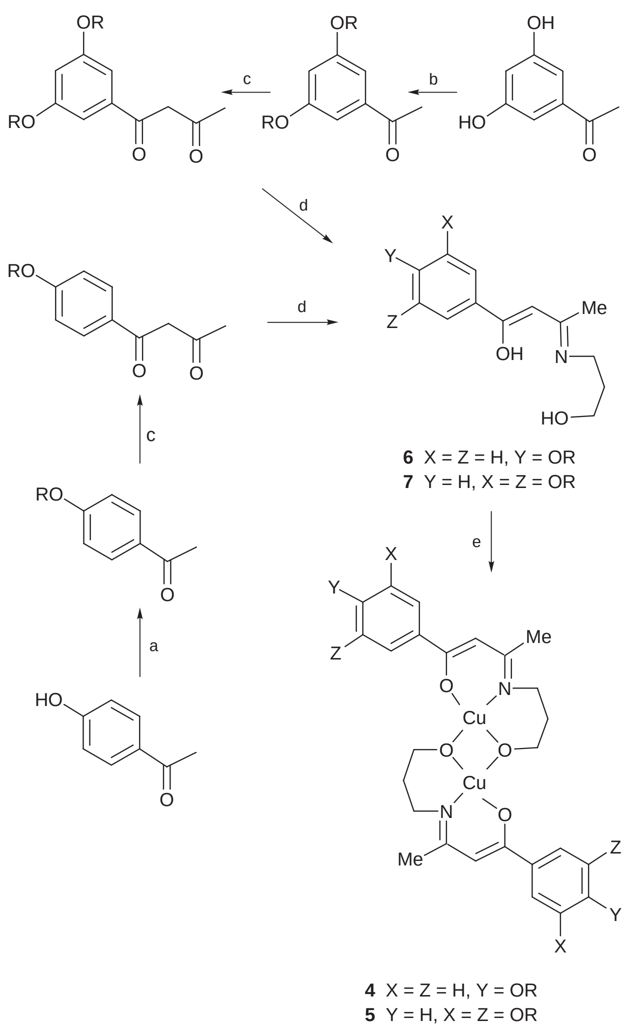


M = Cu, VO
1 Y = H
2 Y = Me

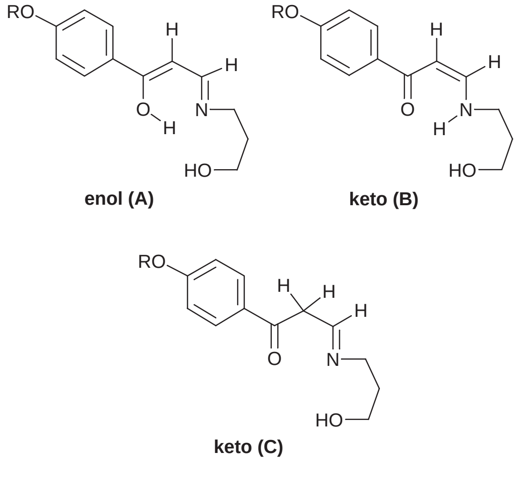
In order to determine the steric influence of the methyl group on the formation of mesophases, we have pursued two similar types of complexes based on β-enaminoketonates and iminopropylketonates. These complexes are very similar in molecular structure, and are all based on a bimetallic core. The preparation, characterization and mesomorphic properties of these complexes, which provided an opportunity to compare systematically the phase behavior in terms of structural differences, will be discussed. The results indicated that the induction of liquid crystallinity were easily achieved by use of a β-enaminoketonate framework. The steric interaction between molecular layers was diminished due to the greater planarity of the central core based on β-enaminoketone instead of β-diketonate.



Scheme 1 R = $(CH_2)_nH$. Reaction conditions: (a) RBr (1.1 equivalents), K_2CO_3 (3.0 equivalents), reflux in MeCOMe, 12 h, yield 79–88%; (b) ethyl formate (4.5 equivalents), Na (3.0 equivalents), stirring in Et_2O at room temperature, 8 h, 71–78%; (c) $NH_2(CH_2)_3OH$ (1.1 equivalents), CH_3CO_2H (3 drops), reflux in CH_2Cl_2, 12 h, 89–95%; (d) $Cu(O_2CMe)_2$ (1.1 equivalents) reflux in thf–MeOH, 12 h, 72–84%



Scheme 2 Reaction conditions: (a) RBr (1.1 equivalents), K_2CO_3 (3.0 equivalents), KI (catalytic), reflux in cyclohexanone, 8 h, yield 80–95%; (b) RBr (2.0 equivalents), K_2CO_3 (4.0 equivalents), KI (catalytic), reflux in cyclohexanone, 12 h, 83–92%; (c) ethyl acetate (1.1 equivalents), NaH (3.0 equivalents), refluxing in dried thf, 8 h, 74–86%; (d) $H_2N(CH_2)_3OH$ (1.1 equivalents), refluxing in $CHCl_3$–EtOH, 12 h, 85–93%; (e) $Cu(O_2CMe)_2$ (1.1 equivalents), refluxing in $CHCl_3$–MeOH, 2 h, 72–84%



Results and Discussion

Synthesis

The synthetic pathways for copper complexes **3** are summarized in Scheme 1. The sodium salts of 3-(4-alkoxyphenyl)-3-oxopropionaldehyde were obtained by Claisen formylation[7] of the appropriate acetophenone, ethyl formate and sodium metal dispersed in diethyl ether. Attempts to isolate 3-(4-alkoxyphenyl)-3-oxopropionaldehydes in neutral form were unsuccessful due to their thermal instability. The Schiff bases 1-(4-alkoxyphenyl)-3-(3-hydroxypropylimino)propan-1-ones were prepared in high yields by reaction of the freshly prepared sodium salts with 3-aminopropan-1-ol in refluxing dichloromethane. The amount of the cyclic compound produced as a major side-product was reduced by use of acetic acid instead of aqueous hydrochloric acid during the neutralization reaction.

These β-enaminoketone-based derivatives are light yellow solids and were characterized by ^1H and ^{13}C NMR spectroscopy. They exist possibly in three different keto–enol tautomeric[8] forms. However, ^1H NMR spectroscopic data in $CDCl_3$ showed three characteristic peaks at δ 5.66, 7.10 and 10.20 assigned to olefinic methine H (H–C=C), aldehyde H (HC=N) and imine H (C=N–H), indicative of the dominance of resonance structure **B**. In addition, the preference for this tautomer was also supported by the characteristic ^{13}C NMR peak at δ *ca.* 189.0 assigned to the keto C=O group. The ratio of different tautomers was mainly dependent on the solvents. The reactions[9] of the Schiff bases with copper acetate monohydrate in refluxing thf–methanol produced complexes **3**. Recrystallization from ethyl acetate or thf–methanol gave yellow-brown solids. These dicopper compounds are all paramagnetic, and their ^1H and ^{13}C NMR spectra display only broad alkoxy signals. All other protons close to the paramagnetic copper centers are not observed.

The synthetic procedures[6] for complexes **4** and **5** are shown in Scheme 2. Condensation reactions of 1-(3,5-dialkoxyphenyl)butane-1,3-diones, obtained from 3,5-dialkoxyacetophenones and ethyl acetate in the presence of NaH, with 3-aminopropan-1-ol in refluxing dry ethanol gave Schiff bases as yellowish solids. The reaction yield is generally high, *ca.* 90–93%. During the work-up about 10% of unchanged β-diketone as the major impurity was separated by column chromatography with methylene dichloride–hexane (3:1) as eluent. These Schiff bases were characterized and confirmed by two characteristic peaks in the ^1H NMR spectra: one sharp singlet at δ *ca.* 5.60 for the olefinic methine hydrogen and another singlet at δ *ca.* 11.45 for the ketone hydroxyl hydrogen. Complexes **4** and **5** were prepared by reactions[9] of the Schiff bases with copper acetate monohydrate in refluxing $CHCl_3$–MeOH overnight. They were isolated as gray solids in good yields after recrystallization from thf–ethyl acetate. They are all soluble in chloroform, hexane, ethyl acetate and thf, and insoluble in alcohol. Satisfactory elemental analyses were obtained and confirmed the bimetallic identity of the complexes.

Mesomorphic properties of copper complexes 3

The liquid crystalline behavior of all the dicopper complexes was studied by thermal analysis (DSC) and polarizing microscopy. The phase transitions and thermodynamic data for **3** are summarized in Table 1. The complexes exhibited enantiotropic behavior, and all have fairly wide mesophase ranges. The crystal-to-mesophase transition was observed in the temperature range 145.0–153.0 °C on heating and the transition enthalpies ranged from 1.34 to 47.7 kJ mol^{-1}. Most complexes have additional crystal-to-crystal transitions. The isotropic points are in the range 163.0–177.0 °C, which are much lower than for most dicopper complexes in the literature.[1c] The mesophase was characteristically identified as smectic A (S_A) based on the optical texture observed. A fan texture on slowly cooling from the isotropic liquid was clearly observed, which is often obtained for rod-like molecules. Also this smectic A phase was easily confirmed by the appearance of a homeotropic texture without subjecting the sample to mechanical stress. In this phase the molecules may spontaneously align normal to the surface, giving a dark, essentially textureless, field between crossed polarizers. The temperature range of the mesophase was *ca.* 18–25 °C on heating and 40–50 °C on cooling.

Table 1 Phase behaviors* of dicopper complexes **3**, **4** and **5**

	n	
3	12	$K_1 \xrightarrow{144.1\ (14.6)} K_2 \underset{114.4\ (19.7)}{\overset{148.3\ (1.34)}{\rightleftharpoons}} S_A \underset{165.4\ (5.39)}{\overset{170.8\ (5.90)}{\rightleftharpoons}} I$
	14	$K_1 \xrightarrow{118.0\ (3.64)} K_2 \underset{120.6\ (58.9)}{\overset{153.0\ (47.7)}{\rightleftharpoons}} S_A \underset{169.5\ (5.85)}{\overset{177.4\ (5.15)}{\rightleftharpoons}} I$
	16	$K_1 \underset{86.4\ (15.3)}{\overset{135.1\ (16.6)}{\rightleftharpoons}} K_2 \underset{119.8\ (21.7)}{\overset{149.4\ (47.7)}{\rightleftharpoons}} S_A \underset{170.0\ (8.12)}{\overset{174.5\ (7.32)}{\rightleftharpoons}} I$
	18	$K_1 \underset{97.2\ (22.8)}{\overset{131.6\ (22.3)}{\rightleftharpoons}} K_2 \underset{117.1\ (20.9)}{\overset{144.7\ (33.9)}{\rightleftharpoons}} S_A \underset{158.2\ (6.69)}{\overset{163.1\ (6.25)}{\rightleftharpoons}} I$
4	8	$K \underset{205.2\ (41.0)}{\overset{215.3\ (43.5)}{\rightleftharpoons}} I$
	12	$K \underset{168.5\ (59.8)}{\overset{179.3\ (62.4)}{\rightleftharpoons}} I$
	16	$K \underset{162.1\ (48.1)}{\overset{172.5\ (44.8)}{\rightleftharpoons}} I$
5	12	$K \underset{86.5\ (87.4)}{\overset{104.0\ (84.5)}{\rightleftharpoons}} I$
	16	$K \underset{64.4\ (139.2)}{\overset{83.0\ (126.4)}{\rightleftharpoons}} I$

* n = Number of carbons in the sidechain; K_1, K_2 = crystal phase; S_A = smectic A phase; I = isotropic. The transition temperature (°C) and enthalpies (in parentheses, kJ mol^{-1}) were determined by DSC at a scan rate of 10.0 °C min^{-1}.

Mesomorphic properties of complexes 4 and 5

These complexes were prepared and studied better to understand the structural relationships in terms of the mesomorphic properties. They have similar structures to complexes **3**, and are all based on iminopropyl ketonate derivatives in which a methyl group is attached to the core group instead of the H atom in **3**. The phase transitions are given in Table 1. Interestingly they all exhibited crystalline phases, and only the crystal-to-isotropic transitions were observed. The molecular shapes of these complexes are likely between rod- and lath-like depending on the number and length of the sidechains. The mesomorphic properties of complexes **3**, **4** and **5** indicated that the formation of liquid crystallinity was not induced or improved by increasing the number of flexible sidechains or/and their length. In order further to elucidate this the copper complex of 2-(3-hydroxypropyl)iminopropyl 3,4,5-tris(dodecyloxy)phenyl ketone (X = Y = Z = $OC_{12}H_{25}$) was also prepared. A crystal-to-isotropic transition at 99.5 °C was observed. The lack of liquid crystallinity in this type of extended bimetallic core group is ascribed to the presence of the terminal methyl group attached to the core group. Mesophase formation is totally suppressed; presumably the steric bulk of a T_d methyl group[3,4] destroyed the weak intermolecular force necessary to induce and/or stabilize the liquid crystallinity. This phenomenon has been observed in other systems. Alternatively, a stable mesophase of ordered hexagonal (Col_h) arrangement was formed in similar copper complexes[6] of 3,5-bis(3,4,5-trialkoxybenzyloxy)phenyl 2-(3-hydroxypropyl)iminopropyl ketones, in which the interlayer distance due to the methyl group was relatively reduced by bulkier and longer substituents at the 3,5 positions of the phenyl group.

Crystal and molecular structures

A single-crystal structure analysis was performed at room temperature for copper complex **5** (n = 8). The green crystals were grown at a thf–MeOH (2:3) interface, and this complex showed only a crystalline phase. Fig. 1 shows the molecular

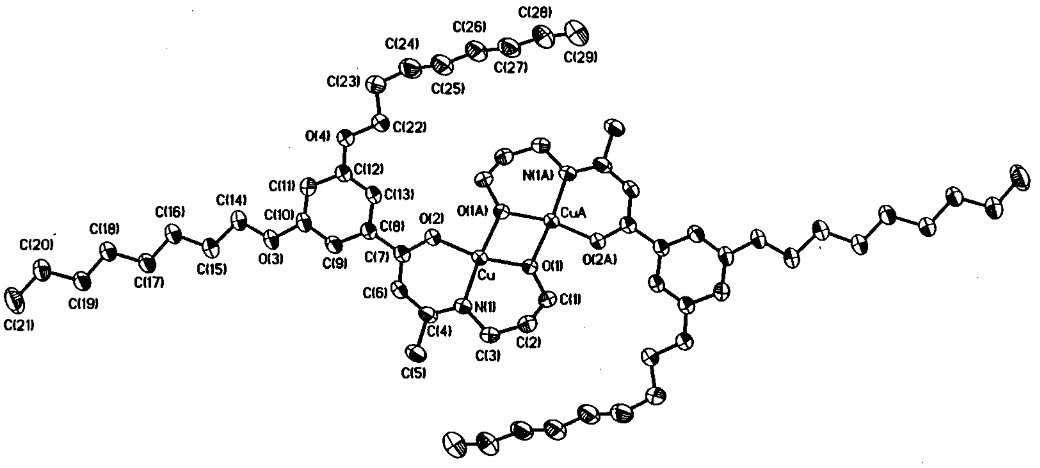


Fig. 1 An ORTEP[10] drawing for copper complex **5** (n = 8) with the atomic numbering scheme

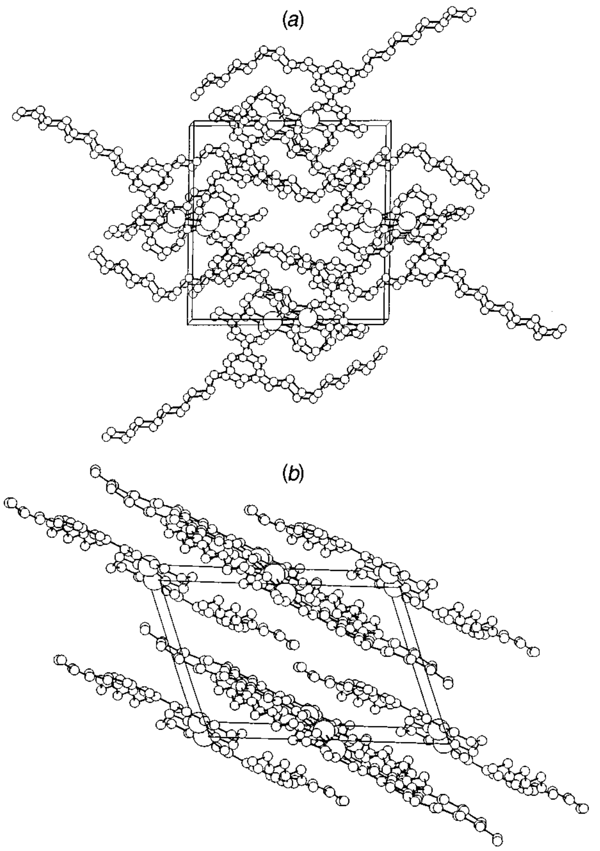


Fig. 2 Two different views of the crystal packing approximately down (*a*) the *a* axis and (*b*) the *c* axis

Table 2 Crystallographic data and structure refinement for bis[3,5-dioctanoylphenyl 2-(3-hydroxypropyl)iminopropyl ketonato]copper(II)

Empirical formula	$C_{58}H_{94}Cu_2N_2O_8$
M	1074.43
T/K	295(2)
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	11.6585(3)
b/Å	15.6227(4)
c/Å	16.7433(5)
β/°	109.12(1)
U/Å^3, *Z*	2881.33(14), 2
D_c/Mg m^{-3}	1.238
Crystal size/mm	0.40 × 0.40 × 0.2
λ/(Mo-Kα)/Å	0.710 73
θ Range for data collection/°	1.83 to 27.50
Reflections collected	53 057
Independent reflections	6611 (R_{int} = 0.0588)
Final *R*1, *wR*2	0.0456, 0.0993

structure with the atomic numbering scheme, and Table 2 the crystallographic and structure refinement data for the molecule. The overall molecular shape is lath-like and nearly flat, with two copper atoms lying 3.0375(5) Å apart, one 0.018 Å above and the other 0.018 Å below the molecular plane defined by atoms N(1), O(2), O(1a) and O(1). The two angles of O(2)–Cu–N(1) and N(1)–Cu–O(1) are of 95.62(7) and 98.19(7)°, which show a small deviation from the ideal angle of 90° expected for a square-planar complex. The molecule is more lath-like than rod-like. The length [from C(21) to C(21A)] and the width [from C(29) to C(29A)] of the molecule are 37.17 and 16.436 Å (Table 3), respectively. Two different views of the crystal packing showing the layered structures are presented in Fig. 2, and reveal that the molecules are packed in a highly interdigitated layered structure.

Table 3 Bond lengths (Å) and angles (°) for bis[3,5-dioctanoylphenyl 2-(3-hydroxypropyl)iminopropyl ketonato]copper(II)

Cu–O(2)	1.888(2)	Cu–O(1)	1.902(2)
Cu–O(1A)	1.941(2)	Cu–N(1)	1.946(2)
Cu · · · CuA	3.0375(5)	O(1)–C(1)	1.409(3)
O(1)–CuA	1.941(2)	O(2)–C(7)	1.284(2)
O(3)–C(10)	1.368(3)	O(3)–C(14)	1.429(3)
O(4)–C(12)	1.369(3)	O(4)–C(22)	1.428(3)
N(1)–C(4)	1.316(3)	N(1)–C(3)	1.475(3)
C(1)–C(2)	1.505(3)	C(2)–C(3)	1.500(3)
C(4)–C(6)	1.410(3)	C(4)–C(5)	1.519(3)
C(6)–C(7)	1.374(3)	C(7)–C(8)	1.500(3)
O(2)–Cu–O(1)	165.97(7)	O(2)–Cu–O(1A)	90.65(6)
O(1)–Cu–O(1A)	75.56(7)	O(2)–Cu–N(1)	95.62(7)
O(1)–Cu–N(1)	98.19(7)	O(1A)–Cu–N(1)	173.73(7)
O(2)–Cu–CuA	127.93(5)	O(1)–Cu–CuA	38.23(4)
O(1A)–Cu–CuA	37.33(4)	N(1)–Cu–CuA	136.42(6)
C(1)–O(1)–Cu	126.42(14)	C(1)–O(1)–CuA	128.23(14)
Cu–O(1)–CuA	104.44(7)	C(7)–O(2)–Cu	125.50(2)
C(10)–O(3)–C(14)	119.90(2)	C(12)–O(4)–C(22)	117.70(2)
C(4)–N(1)–C(3)	117.70(2)	C(4)–N(1)–Cu	122.40(2)
C(3)–N(1)–Cu	119.80(2)	O(1)–C(1)–C(2)	110.90(2)
C(3)–C(2)–C(1)	115.20(2)	N(1)–C(3)–C(2)	114.00(2)
N(1)–C(4)–C(6)	123.70(2)	N(1)–C(4)–C(5)	121.00(2)
O(2)–C(7)–C(6)	124.00(2)	O(2)–C(7)–C(8)	114.80(2)

Symmetry transformation used to generate equivalent atoms: A 1 $-x$, $-y$, $-z + 1$.

Conclusion

Two different types of structurally similar copper complexes were prepared and used to demonstrate the effect of a steric methyl group on liquid crystalline behavior. A mesophase was easily formed by use of a more planar structure. The presence of the methyl group close to the central core caused a severe distortion from planarity of the molecules, which prevents mesogenic behavior. On the other hand the mesomorphism can be greatly improved by reducing the steric interference resulting from any sterically unfavorable groups attached to the central core.

Experimental

All reaction chemicals were reagent grade from Aldrich Chemical Co., used without further purification. Tetrahydrofuran was dried over sodium–benzophenone, other solvents were purified and dried by standard techniques. Proton and ^{13}C NMR spectra were measured on a Bruker DRS-200 spectrometer, infrared spectra on a Bio-Rad FTS-155 using polystyrene as a standard and Nujol mulls between two KBr plates. The DSC thermographs were carried out on a Perkin-Elmer DSC-7 calibrated with a pure indium sample at 156 °C. Optical polarized microscopy was performed on a Nikkon MICROPHOT-FXA instrument with a Mettler FP90/FP82HT hot-stage system. Elemental analyses for carbon, hydrogen and nitrogen were conducted on a Heraeus CHN-O-Rapid elemental analyzer, and the results are listed in Table 4. 4-Alkoxyacetophenones, 3,5-dialkoxyacetophenones, 1-(4-alkoxyphenyl)butane-1,3-diones and 1-(3,5-dialkoxyphenyl)-butane-1,3-diones were prepared according to literature procedures.[5,6]

Preparations

4-Dodecyloxyacetophenone. This compound was prepared by literature methods.[5,6] White crystals, yield 79%. ^{1}H NMR ($CDCl_3$): δ 0.82 (t, CH_3, 3 H), 1.23–1.77 (m, CH_2, 20 H), 2.43 (s, $COCH_3$, 3 H), 3.95 (t, OCH_3, 2 H), 6.84 (d, C_6H_4, 2 H) and 7.86 (d, C_6H_4, 2 H). ^{13}C NMR ($CDCl_3$): δ 13.98, 22.20, 22.56, 25.87, 26.05, 27.86, 27.99, 29.01, 29.25, 29.45, 31.78, 68.10, 113.90, 129.98, 130.50, 162.96 and 196.56.

Table 4 Elemental analyses of dicopper complexes with calculated values in parentheses

Compound	*n*	Analysis (%) C	H	N
3	12	64.23 (63.90)	8.30 (8.27)	3.12 (3.10)
	14	64.96 (65.17)	8.52 (8.62)	2.75 (2.92)
	16	65.85 (66.30)	8.70 (8.94)	2.66 (2.76)
	18	67.44 (67.32)	9.36 (9.23)	2.67 (2.62)
5	12	68.65 (68.43)	9.99 (9.78)	2.17 (2.16)
	16	71.09 (70.96)	10.57 (10.45)	1.91 (1.84)
4	8	61.85 (61.67)	7.66 (7.64)	3.45 (3.43)
	12	64.61 (64.56)	8.58 (8.45)	3.11 (3.01)
	16	67.11 (66.82)	9.23 (9.09)	2.71 (2.69)

β-Enaminoketones. 1-(4-*Dodecyloxyphenyl*)-3-(3-*hydroxypropylimino*)*propan*-1-*one*. Sodium metal (0.75 g, 32.6 mmol) was freshly cut into small pieces and stirred in dry diethyl ether (25 cm^3) for 0.5 h. A mixture of 4-dodecyloxyacetophenone (5.0 g, 16.45 mmol) in diethyl ether (20 cm^3) and ethyl formate (6.60 cm^3, 16.45 mmol) was slowly added and allowed to stir at room temperature under a nitrogen atmosphere for 12 h. The solution was concentrated to give a light greenish solid mixed with some sodium metal. Methanol was slowly added to quench the sodium metal, and the solution filtered to remove inorganic salts. It was transferred to a round-bottom flask (250 cm^3), and then neutralized with acetic acid. At this time the solution turned from cloudy yellow to clear red. 3-Aminopropan-1-ol (1.06 g, 16.45 mmol) was added dropwise and the mixture gently refluxed for 24 h. It was concentrated in vacuum to give the crude product as a brown solid. A light orange solid was obtained after recrystallization from hexane–dichloromethane (9:1). Yield 96%. ^{1}H NMR ($CDCl_3$): δ 0.88 (t, CH_3, 3 H), 1.15–1.86 (m, CH_2, 20 H), 3.44 (q, OCH_2, 2 H), 3.78 (t, NCH_2, 2 H), 4.01 (t, OCH_2, 2 H), 5.66 (d, CH_2, 1 H), 6.89 (d, C_6H_4, 2 H), 7.10 (t, CHN, 1 H), 7.30 (d, C_6H_4, 2 H) and 10.20 (t, CNH, 1 H). ^{13}C NMR ($CDCl_3$): δ 14.13, 22.72, 25.87, 29.21, 31.93, 33.35, 45.75, 59.43, 68.14, 89.71, 113.92, 128.87, 132.24, 153.98, 161.54 and 189.15. IR (thin film): 3420, 2941, 2848, 1663, 1606, 1586, 1532, 1490, 1478, 1382, 1297, 1254, 1173, 1115, 1069, 1019, 853 and 780 cm^{-1}.

3,5-*Bis*(*dodecyloxy*)*acetophenone*. White crystals, yield 83%. ^{1}H NMR ($CDCl_3$): δ 0.82 (t, CH_3, 6 H), 1.25–1.80 (m, CH_2, 40 H), 2.51 (s, $COCH_3$, 3 H), 3.93 (t, OCH_2, 4 H), 6.59 (s, C_6H_3, 1 H) and 7.02 (s, C_6H_3, 2 H). ^{13}C NMR ($CDCl_3$): δ 14.00, 22.59, 25.96, 26.55, 29.17, 29.28, 31.75, 68.17, 105.97, 106.45, 138.80, 160.25 and 197.58.

1-(4-*Dodecyloxyphenyl*)*butane*-1,3-*dione*. Yellow solid, yield 79%. ^{1}H NMR ($CDCl_3$): δ 0.85 (s, CH_3, 3 H), 1.24–1.78 (m, CH_2, 20 H), 2.10 (s, $COCH_3$, 3 H), 3.97 (t, OCH_2, 2 H), 6.06 (s, COHCH, 1 H), 6.88 (d, C_6H_4, 2 H), 7.87 (d, C_6H_4, 2 H) and 16.32 (s, COHCH, 1 H). ^{13}C NMR ($CDCl_3$): δ 14.04, 22.63, 25.14, 25.94, 29.09, 29.32, 29.51, 31.85, 68.09, 95.61, 114.32, 127.21, 129.03, 162.70, 184.12 and 191.36.

1-[3,5-*Bis*(*dodecyl*)*oxyphenyl*]*butane*-1,3-*dione*. Yellow solid, yield 77%. ^{1}H NMR ($CDCl_3$): δ 0.81 (s, CH_3, 6 H), 1.24–1.82 (m, CH_2, 40 H), 2.05 (s, $COCH_3$, 3 H), 3.91 (t, OCH_2, 4 H), 6.03 (s, COHCH, 1 H), 6.53 (t, C_6H_3, 1 H), 6.93 (t, C_6H_3, 2 H) and 16.10 (s, COHCH, 1 H). ^{13}C NMR ($CDCl_3$): δ 13.99, 19.61, 22.59, 25.41, 25.98, 29.12, 29.23, 29.18, 29.65, 31.76, 68.17, 96.68, 105.28, 105.37, 136.76, 160.28, 183.65 and 192.93.

Schiff bases of iminopropyl ketones. 4-*Dodecyloxyphenyl* 2-(3-*hydroxypropyl*)*iminopropyl ketone*. 1-(4-Dodecyloxyphenyl)-butane-1,3-dione (3.0 g, 8.7 mmol), 3-aminopropan-1-ol (0.73 cm^3, 9.6 mmol) and glacial acetic acid (0.20 cm^3) were mixed in dried thf (100 cm^3) under a nitrogen atmosphere. The mixture was refluxed for 24 h then concentrated to give a brown crude solid. The product was purified by chromatography eluting with methylene chloride–hexane (3:1 v/v). Evaporation of the solvent gave the product as a light yellow solid which was recrystallized from thf–MeOH. Yield 90%. ^{1}H NMR ($CDCl_3$): δ 0.85 (t, CH_3, 3 H), 1.24–1.81 (m, CH_2, 20 H), 1.95 (s, $CNCH_3$, 3 H), 3.33 (q, CH_2OH, 2 H), 3.68 (t, NCH_3 2 H), 3.92 (t, OCH_2, 2 H), 5.55 (s, COHCH, 1 H), 6.83 (d, C_6H_3, 2 H), 7.76 (d, C_6H_4, 2 H) and 11.25 (s, COHCH, 1 H). ^{13}C NMR ($CDCl_3$): δ 14.03, 19.21, 22.53, 25.14, 29.08, 29.18, 29.31, 29.40, 31.79, 32.51, 39.82, 59.04, 67.89, 91.42, 113.75, 128.46, 132.57, 161.08, 164.80 and 186.67.

3,5-*Bis*(*dodecyloxy*)*phenyl* 2-(3-*hydroxypropyl*)*iminopropyl ketone*. Light yellow solid, yield 89%. ^{1}H NMR ($CDCl_3$): δ 0.79 (t, CH_3, 6 H), 1.24–1.80 (m, CH_2, 40 H), 1.96 (s, $CNCH_3$, 3 H), 3.34 (q, CH_2OH, 2 H), 3.65 (t, NCH_3, 2 H), 3.93 (t, OCH_2, 4 H), 5.53 (s, COHCH, 1 H), 6.45 (s, C_6H_3, 1 H), 6.91 (s, C_6H_3, 2 H) and 11.32 (s, COHCH, 1 H). ^{13}C NMR ($CDCl_3$): δ 14.12, 19.35, 21.03, 22.69, 26.04, 29.36, 29.63, 31.92, 32.47, 39.96, 59.45, 60.41, 68.16, 92.27, 103.83, 105.16, 142.46, 160.08, 165.34 and 187.24.

Copper complexes of 1-(4-alkoxyphenyl)-3-(3-hydroxypropylimino)propan-1-one 3. A solution of 1-(4-dodecyloxyphenyl)-3-(3-hydroxypropylimino)propan-1-one (0.30 g, 0.77 mmol) dissolved in dichloromethane (10 cm^3) was added to a hot methanol solution (10 cm^3) of copper acetate monohydrate (0.158 g, 0.79 mmol). The mixture was stirred at room temperature for 1 h and then gently refluxed for 1 h. The crude green solid was collected and then recrystallized from dichloromethane–methanol (2:3) to give a light green solid. Yield 78%. IR (thin film): 3458, 2929, 2840, 1606, 1532, 1505, 1463, 1432, 1389, 1297, 1243, 1181, 1173, 1092, 1019, 845, 718 and 617 cm^{-1}.

Bis[3,5-dialkoxyphenyl 2-(3-hydroxypropyl)iminopropyl ketonato]copper(II) complexes 5. To a stirred solution of 3,5-bis(dodecyloxy)phenyl 2-(3-hydroxypropyl)iminopropyl ketone (0.30 g, 0.53 mmol) in dichloromethane (10 cm^3) was added a solution of copper acetate monohydrate (0.11 g, 0.55 mmol) in hot methanol (5.0 cm^3). The reaction mixture was stirred for 1 h and then gently refluxed for 2 h. The mixture was concentrated to give a brown-green solid. The green-gray product was obtained by recrystallization from ethyl acetate–methanol. Yield 83%. IR (thin film): 3440, 2936, 2848, 1576, 1516, 1457, 1416, 1349, 1300, 1274, 1268, 1167, 1100, 1051, 998, 965, 937, 917, 838, 770, 723 and 615 cm^{-1}.

Crystal-structure determination of complex 5 ($n = 8$)

Single-crystal X-ray diffraction data were measured on a Seimens SMART CCD diffractometer. Reflections were collected using four different φ setting angles, each setting covers a ω range of 180° with a 0.3° interval between frames. Each frame was exposed for 20 s. The detector was located 4.0 cm away from the crystal. An empirical absorption correction was applied. The structure was solved by direct methods. Hydrogen atoms were fixed at calculated positions and refined using a riding model. Anisotropic displacement parameters were used for all non-H atoms, while the given isotropic displacement parameters were used for H atoms (1.2 and 1.5 times the equivalent isotropic displacement parameter of the atom to which they are attached respectively for methylene H atoms and methyl H atoms).

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