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Hexagonal columnar mesophases in oxygen-bridged dicopper complexes

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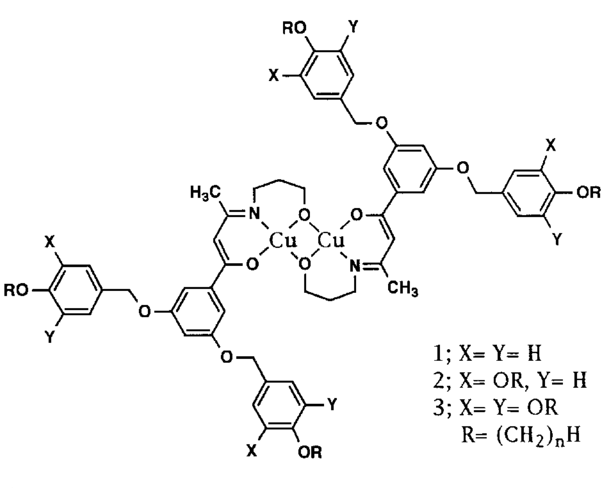
The synthesis of a series of bidentate Schiff's bases; 3,5-bis(3′,4′,5′-trialkoxybenzyloxy)phenyl-2-*N*-(3-hydroxypropy)iminopropyl ketone, and their dicopper complexes are reported. The liquid crystalline behaviour of these dicopper complexes was studied by DSC, polarized optical microscopy and X-ray diffraction. The phases were characterized and identified as hexagonal columnar (D_h) phases, which are typical of disc-like molecules.

1. Introduction

Coordination compounds are the largest category among metallomesogenic materials [1–4]. A variety of novel geometric structures created by incorporation of metal centres result in the generation of new materials and the formation of interesting physical properties. Incorporating paramagnetic metal centres has the potential to generate magnetic materials if bulk spin alignment can be induced. In bimetallic liquid crystals [5–9] the interactions between the metal centres play an important role, not only in the formation of the mesophases, but also in the induction of the resultant properties. The design and synthesis of molecular systems able to incorporate multiple metal centres still remains a major challenge. In this work, the formation of discotic phases based on copper complexes of iminopropyl ketone is discussed, and to the best of our knowledge this represents the first hexagonal discotic (D_h) observed for this type of bimetallic liquid crystal.

2. Experimental

We have prepared a number of dicopper complexes shown in scheme 1. The typical synthetic procedures for these metal complexes are summarized in scheme 2. Condensation reactions of 1-[3′,5′-di(3″,4″,5″-trialkoxybenzyloxyphenyl)]butane-1,3-dione† with 3-amino-1-propanol in dry ethanol heated at reflux gave the Schiff's bases 3,5-bis(3′,4′,5′-trialkoxybenzyloxy)phenyl-2-*N*-(3-hydroxypropy)iminopropyl ketone‡ as yellowish solids or oily pastes depending on the length of the alkoxy chains. The dicopper complexes were prepared by the reaction [10, 11] of the Schiff's bases and copper acetate in $CHCl_3/CH_3OH$ heated at reflux. Satisfactory elemental analyses of the grey–greenish compounds were obtained after recrystallization from THF/CH_3OH (see table 1).



Scheme 1.

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† 1-(3′,5′-Di(3″,4″,5″-tridecanoxybenzoxyphenyl)butane-1,3-dione; yield: 76 per cent, yellow oil. ^{1}HNMR (ppm, $CDCl_3$): 0·86 (t, $-CH_3$, 18 H), 1·21–1·81 (m, $-(CH_2)_{48}$, 96 H), 2·16 (s, $-COCH_3$, 3 H), 3·96 (tt, $-OCH_2$, 12 H), 4·93 (s, $-OCH_2C_6H_2$, 4 H), 6·07 (s, –COCH–CH, 1 H), 6·60 (s, $-C_6H_2$, 4 H), 6·73 (t, $-C_6H_3$, 1 H), 7·10 (d, $-C_6H_3$, 2 H), 16·08 (s, –COHCH, 1 H), ^{13}CNMR($CDCl_3$): 14·10, 23·71, 26·18, 29·40, 29·46, 29·67, 29·82, 30·40, 31·97, 69·20, 70·82, 73·48, 96·96, 106·2, 106·3, 131·3, 137·1, 138·2, 153·4, 160·1, 183·6, 193·1.

‡ 3,5-Bis(3′,4′,5′-tridecanoxybenzyloxy)phenyl-2-*N*-(3-hydroxypropyl)iminopropyl ketone; yield: 82 per cent, yellow oil. ^{1}H NMR (ppm, $CDCl_3$): 0·86 (t, $-CH_3$, 18 H), 1·24–1·83 (m, $-(CH_2)_{48}$, 98 H), 2·01 (s, $-CNCH_3$, 3 H), 3·43 (q, $-CH_2OH$, 2 H), 3·73 (t, $-NCH_2$, 2 H), 3·96 (tt, $-OCH_2$, 12 H), 4·94 (s, $-OCH_2C_6H_2$, 4 H), 5·59 (s, –COCH–CH, 1 H), 6·60 (s, $-C_6H_2$, 4 H), 6·74 (t, $-C_6H_3$, 1 H), 7·14 (d, $-C_6H_3$, 2 H), 11·44 (s, –COHCH, 1 H). ^{13}C NMR ($CDCl_3$): 14·10, 23·71, 26·18, 29·40, 29·46, 29·67, 29·82, 30·40, 31·97, 40·00, 59·58, 69·14, 70·68, 73·46, 92·25, 104·4, 105·9, 106·3, 131·7, 138·0, 142·7, 153·3, 159·8, 165·4, 186·9.

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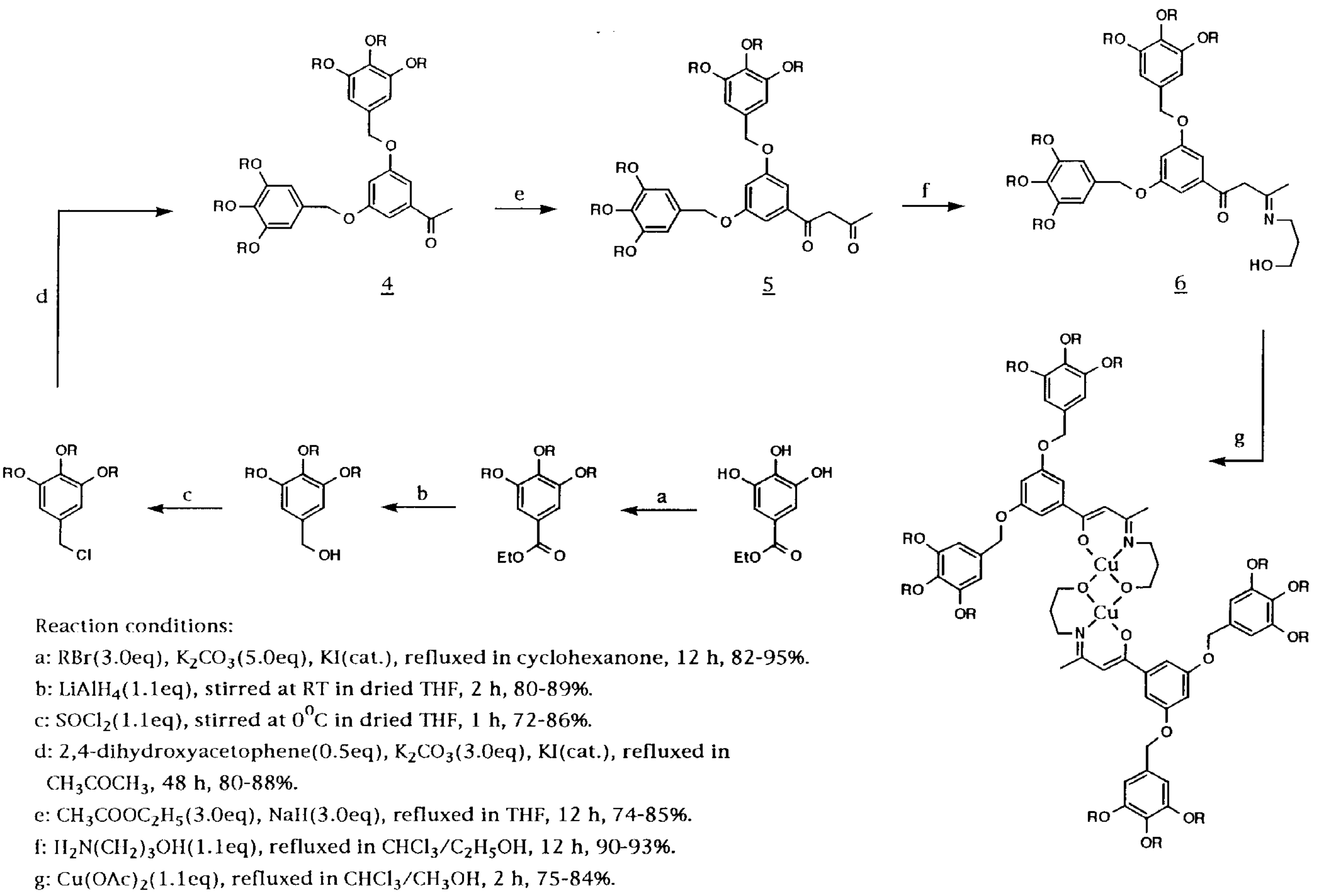

Reaction conditions:

a: RBr(3.0eq), K_2CO_3(5.0eq), KI(cat.), refluxed in cyclohexanone, 12 h, 82-95%.

b: $LiAlH_4$(1.1eq), stirred at RT in dried THF, 2 h, 80-89%.

c: $SOCl_2$(1.1eq), stirred at 0^oC in dried THF, 1 h, 72-86%.

d: 2,4-dihydroxyacetophene(0.5eq), K_2CO_3(3.0eq), KI(cat.), refluxed in CH_3COCH_3, 48 h, 80-88%.

e: $CH_3COOC_2H_5$(3.0eq), NaH(3.0eq), refluxed in THF, 12 h, 74-85%.

f: $H_2N(CH_2)_3OH$(1.1eq), refluxed in $CHCl_3/C_2H_5OH$, 12 h, 90-93%.

g: $Cu(OAc)_2$(1.1eq), refluxed in $CHCl_3/CH_3OH$, 2 h, 75-84%.

Scheme 2.

Table 1. Elemental analyses of dicopper complexes of series 3.

R	Elemental analysis/per cent			
C_5H_{11}	Calcd.	C=67·79	H=8·68	N=1·38
	Found	C=67·77	H=8·76	N=1·37
C_6H_{13}	Calcd.	C=69·16	H=9·12	N=1·28
	Found	C=69·01	H=9·13	N=1·32
C_7H_{15}	Calcd.	C=70·34	H=9·49	N=1·19
	Found	C=70·30	H=9·55	N=1·21
C_8H_{17}	Calcd.	C=71·36	H=9·82	N=1·11
	Found	C=71·40	H=9·85	N=1·13
$C_{10}H_{21}$	Calcd.	C=73·04	H=10·35	N=0·98
	Found	C=72·86	H=10·39	N=1·01
$C_{12}H_{25}$	Calcd.	C=74·36	H=10·78	N=0·88
	Found	C=74·33	H=10·91	N=0·89
$C_{14}H_{29}$	Calcd.	C=75·43	H=11·12	N=0·79
	Found	C=75·57	H=11·28	N=0·80
$C_{16}H_{33}$	Calcd.	C=76·32	H=11·46	N=0·72
	Found	C=76·38	H=11·51	N=0·69

3. Results and discussion

The phase behaviour of the dicopper complexes was characterized by DSC and polarized optical microscopy. Complexes of series **1** and **2** exhibited only crystalline phases. The phase transitions of the dicopper complexes of series **3** are given in table 2. Complex **3** ($n=5$) exhibited only a crystalline phase. However, derivatives with longer side chain carbon lengths ($n=6,7,8,10$ and 12) showed liquid crystallinity. The mesophases were identified as columnar discotic phases which are usually expected for disc-like molecules. The DSC analysis of the copper complexes of series **3** showed a crystal-to-discotic-to-isotropic (Cr–D–I) phase behaviour. These metal complexes melt to give birefringent fluid phases ($\Delta H=7{\cdot}0$–$10{\cdot}0\,\mathrm{kcal\,mol^{-1}}$, 29·3–41·9 kJ $\mathrm{mol^{-1}}$) at a surprisingly low temperature (88·0–100°C) and the clearing transitions ($\Delta H=3{\cdot}50$–$6{\cdot}60\,\mathrm{kcal\,mol^{-1}}$, 14·6–27·6 kJ $\mathrm{mol^{-1}}$) ranged from 107·0 to 117·0°C. The temperature ranges of the mesophases are fairly narrow, slightly side chain dependent, and vary from 5·0 to 30·0°C. Mosaic textures with linear birefrigent defects and large areas of uniform homeotropic alignment were observed by slow cooling from the isotropic phase.

The identification of the columnar hexagonal discotic phases was also confirmed by variable-temperature X-ray powder diffraction (XRD). The copper complex **3** ($n=10$) displayed a diffraction pattern of a two-

Table 2. Phase transition temperatures (°C) and enthalpies (in parentheses/kJ mol^{-1}) of the dicopper complexes of series **3** determined by DSC (5·0°C min^{-1}). *n* denotes the length of the alkoxy chains.

n	Phase transitions
5	$\mathrm{Cr}\ \underset{106\cdot6\ (90\cdot0)}{\overset{117\cdot2\ (88\cdot3)}{\rightleftarrows}}\ \mathrm{I}$
6	$\mathrm{Cr}\ \underset{62\cdot8\ (33\cdot03)}{\overset{92\cdot9\ (37\cdot05)}{\rightleftarrows}}\ \mathrm{D_h}\ \underset{102\cdot7\ (14\cdot82)}{\overset{107\cdot2\ (15\cdot37)}{\rightleftarrows}}\ \mathrm{I}$
7	$\mathrm{Cr}\ \underset{73\cdot3\ (41\cdot16)}{\overset{87\cdot7\ (39\cdot31)}{\rightleftarrows}}\ \mathrm{D_h}\ \underset{112\cdot7\ (23\cdot06)}{\overset{116\cdot9\ (23\cdot66)}{\rightleftarrows}}\ \mathrm{I}$
8	$\mathrm{Cr}\ \underset{82\cdot0\ (29\cdot73)}{\overset{93\cdot2\ (28\cdot89)}{\rightleftarrows}}\ \mathrm{D_h}\ \underset{110\cdot5\ (18\cdot55)}{\overset{115\cdot0\ (20\cdot10)}{\rightleftarrows}}\ \mathrm{I}$
10	$\mathrm{Cr}\ \underset{89\cdot7\ (33\cdot58)}{\overset{99\cdot5\ (32\cdot20)}{\rightleftarrows}}\ \mathrm{D_h}\ \underset{107\cdot1\ (26\cdot63)}{\overset{111\cdot9\ (27\cdot72)}{\rightleftarrows}}\ \mathrm{I}$
12	$\mathrm{Cr}\ \underset{88\cdot2^{a}}{\overset{83\cdot1^{a}}{\rightleftarrows}}\ \mathrm{D_h}\ \underset{92\cdot6^{a}}{\overset{97\cdot0^{a}}{\rightleftarrows}}\ \mathrm{I}$
14	$\mathrm{Cr}\ \underset{81\cdot8\ (41\cdot24)}{\overset{91\cdot6\ (41\cdot70)}{\rightleftarrows}}\ \mathrm{I}$
16	$\mathrm{Cr}\ \underset{73\cdot5\ (36\cdot09)}{\overset{84\cdot7\ (35\cdot00)}{\rightleftarrows}}\ \mathrm{I}$

Cr, crystal; $\mathrm{D_h}$, hexagonal discotic; I, isotropic phase.
[a]Unresolved peaks.

dimensional hexagonal lattice with a strong peak at 33·19 Å and three weak peaks at 16·68 Å, 11·13 Å and 8·35 Å. In addition, the observation of a distinct peak at 3·81 Å indicated a relatively ordered mesophase. This peak refers to a more regular period within the columns than many $\mathrm{D_h}$ systems. However, also at a wide angle we observed liquid-like correlations of 5·30–4·74 Å. A temperature dependence of the lattice parameters was also observed in these metal complexes. We found that the low angle reflections of the copper complex **3** (n= 7) generally shift to a larger *d*-spacing with decreasing temperature; 30·04 Å at 100°C to 30·68 Å at 90°C, thereby indicating a lattice expansion.

Future research will be focused on studies of related physical properties of these dicopper complexes as well as other dimetallic complexes, particularly in understanding the effects of two metal centres on liquid crystallinity.

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