

# Discotic bimetalloenesogens: highly disordered mesophases of columnar hexagonal arrangements in bis(tetraketone) vanadyl and copper complexes †

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A series of bis(tetraketone) complexes of dicopper and divanadyl has been prepared and their mesomorphic properties investigated by polarized optical microscopy and powder X-ray diffraction.

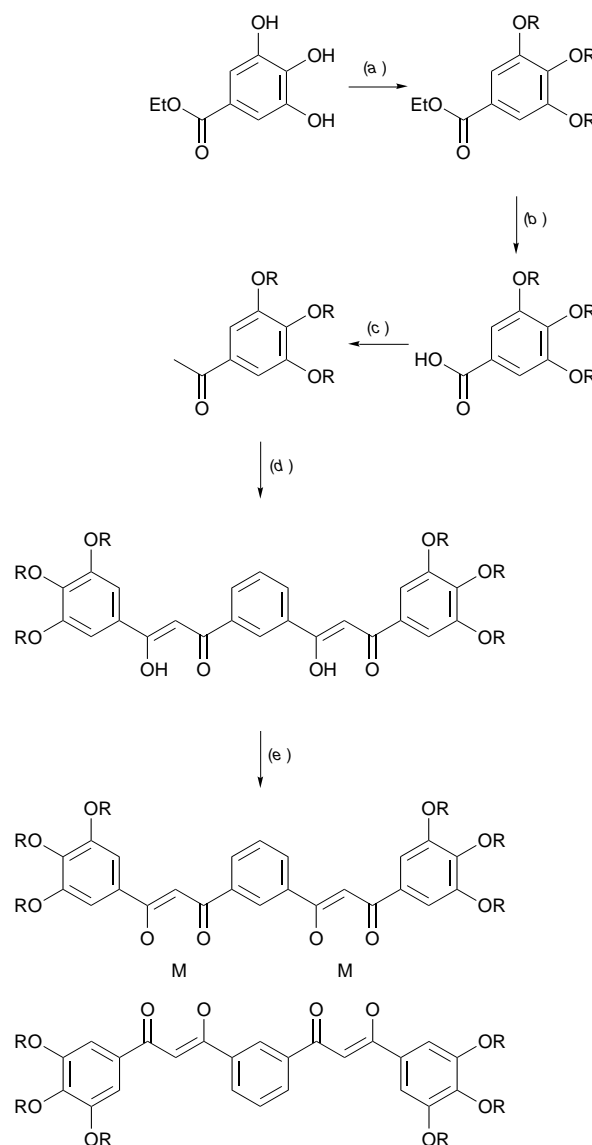
Molecular design and synthesis of new metal complexes with novel mesophases and/or physical properties represent an active research area in metallomesogenic materials.<sup>1</sup> The incorporation of a metal or metal centres can not only lead to new structures and geometries capable of generating new mesogenic materials,<sup>1,2</sup> but also results in interesting electrical, optical and magnetic properties. In bimetallic liquid crystals the interaction between metal centres in molecular structures, whether in close proximity or remote from each other, may influence the formation of liquid-crystalline mesophases, and consequently determines the physical properties of these complexes. However, this approach to an understanding of bimetallic liquid crystals still remain limited, and only a few bimetallic complexes have been prepared<sup>3</sup> and studied. We report herein our results on the development of the first discotic<sup>4</sup> divanadyl and dicopper liquid-crystalline complexes.

We have prepared and characterized a number of bimetallic complexes. The typical synthetic procedures are summarized in Scheme 1. The tetraketones 1,3-bis[3-(3,4,5-trialkoxyphenyl)-3-oxopropanoyl]benzene‡ and 1,3-bis[3-(3,4-dialkoxyphenyl)-3-oxopropanoyl]benzene, were synthesized by condensation of the isophthalic acid dimethyl esters, the appropriate acetophenone derivatives and sodium hydride in refluxing thf or 1,2-dimethoxyethane.

Reactions of the tetraketones with copper acetate and vanadyl sulfate in refluxing  $\text{CHCl}_3$ -MeOH gave the bimetallic tetraketone complexes<sup>5</sup> in high yields. Satisfactory elemental analysis for these metal complexes were obtained after several recrystallizations (SUP 57200).

The mesomorphic properties of these bimetallic complexes are summarized in Table 1. Copper complexes **1a** ( $n = 12$  or 18) showed only crystal phases with isotropic temperatures at ca. 250–300 °C. However, when the number of carbon atoms in the sidechains is greater than ten for complexes **2a** and six for complexes **3a**, the copper complexes exhibited columnar discotic

liquid phases (SUP 57200). Differential scanning calorimetry (DSC) analysis of complexes **2a** and **3a** showed typical discotic phase transitions of crystal-to-discotic-to-isotropic ( $\text{K} \rightarrow \text{D} \rightarrow \text{I}$ ). These copper complexes showed a large enthalpy (88.0–305.0  $\text{kJ mol}^{-1}$ ) for the crystal-to-liquid crystal transitions at lower temperatures (124–132 and 91–120 °C for



**Scheme 1** (a) RBr (3.0 equivalents),  $\text{K}_2\text{CO}_3$  (7.0 equivalents), KI (catalyst) refluxing in MeCOMe, 72 h, 73–94%. (b) KOH (2.0 equivalent), refluxing in tetrahydrofuran (thf)-water (5:1), 12 h, 92–98%. (c) LiMe (2.0 equivalents) stirred in dried thf at room temperature, 12 h, 82–87%. (d) Isophthalic acid dimethyl ester (0.5 equivalents), NaH (3.0 equivalents), refluxing in thf, 4 d, 72–85%. (e)  $\text{Cu}(\text{O}_2\text{CMe})_2$  or  $\text{VOSO}_4$  (1.1 equivalents) refluxing in  $\text{CHCl}_3$ -MeOH, 12 h, 73–83%

† Supplementary data available, (No. SUP 57200, 6 pp.): tables of enthalpies of phase changes and elemental analyses for all compounds reported. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1.

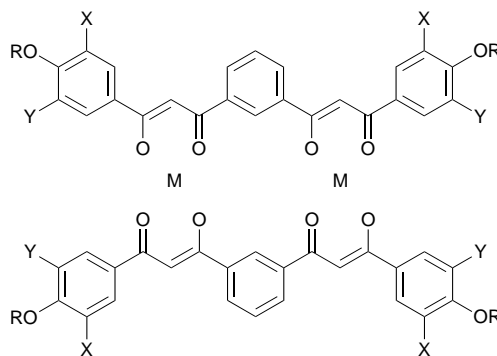
‡ 1,3-bis[3-(3,4,5-tridocenoxyphenyl)-3-oxopropanoyl]benzene: yield, 86%, light yellow solids.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  0.87 (t,  $\text{CH}_3$ , 18 H), 1.29–1.51 (m,  $\text{CH}_2$ , 108 H), 1.76–1.90 (m,  $\text{CH}_2$ , 12 H), 4.06 (t,  $\text{OCH}_2$ , 12 H), 6.83 (s,  $\text{CH}=\text{C}$ , 2 H), 7.19 (s,  $\text{C}_6\text{H}_2$ , 4 H), 7.63 (t,  $\text{C}_6\text{H}_4$ , 1 H), 8.12 (d,  $\text{C}_6\text{H}_4$ , 2 H), 8.58 (s,  $\text{C}_6\text{H}_4$ , 1 H), 17.02 (s, COH, 2 H).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  12.02, 14.71, 19.35, 23.31, 26.74, 30.03, 30.31, 30.99, 32.21, 32.56, 35.29, 36.70, 70.14, 74.26, 93.81, 106.9, 110.7, 126.3, 129.6, 130.9, 131.1, 136.8, 143.5, 153.8, 183.9, 187.5.

complexes **2a** and **3a**) and a low enthalpy (1.13–5.77 kJ mol<sup>-1</sup>) for the liquid crystal-to-isotropic transition at higher temperatures (220–258 and 169–236 °C for complexes **2a** and **3a**), indicating that the mesophases are in highly disordered states. The temperature range of the mesophases is fairly wide and slightly side-chain dependent at about 79–126 °C. Under a polarized microscope these complexes gave pseudo-focal-conic or fan textures with linear birefringent defects and large areas of uniform homeotropic domains.

The vanadyl complexes **3b** showed similar discotic behaviour. Transitions of crystal-to-isotropic phases were only observed for vanadyl complexes **1b** ( $n = 12$ ) and **2b** ( $n = 10, 12$  or  $16$ ). The results revealed that the stronger intermolecular co-ordination between the vanadyl centres inhibited the formation of the liquid-crystal phases. However, increasing the total number of side-chains to 12 (when  $n > 6$ ) in complexes **3b** facilitated the

formation of columnar discotic hexagonal phases as for the copper complexes. The identification of columnar hexagonal discotic phases was confirmed by variable-temperature X-ray powder diffraction (XRD), as shown in Table 2. Complex **3b** ( $n = 12$ ) displays a diffraction pattern of a two-dimensional hexagonal lattice with a strong peak and two weak peaks at 33.15, 19.13 and 16.57 Å. However, complexes **2a** ( $n = 16$ ) exhibited similar diffraction patterns at 34.88, 20.14 and 17.07 Å. These are typically characteristic of a D<sub>hd</sub> phase with a  $d$ -spacing ratio<sup>2a,3a,c</sup> of 1,  $\sqrt{\frac{1}{3}}$  and  $\frac{1}{2}$ , respectively. However, liquid-like correlations between the rigid cores occur at wide angle regions of 5.30–4.64 Å. Temperature dependence of the lattice parameters is also observed in these metal complexes. We find that the low-angle reflections of complexes **3a** ( $n = 16$ ) generally shift to a larger  $d$  spacing with decreasing temperatures, thereby indicating a lattice expansion. Absence of distinct peaks at wide angles is consistent with DSC analysis of low enthalpies of discotic-to-isotropic transitions, indicative of a highly disordered mesophase. The geometry of the divanadyl centres in complexes **1b–3b** either *syn* or *anti*, is uncertain based on IR data. The growth of single crystals for X-ray structural determination is in progress.

In summary, we have discussed our results on the dicopper and divanadyl complexes of tetraketones. Future research will be focused on the study of related physical properties of these bimetallic complexes, particularly in understanding the effects of two remote metal centres on liquid crystallinity.



- 1 X = Y = H  
 2 X = OR, Y = H  
 3 X = Y = OR  
 M = Cu (a) or VO (b)  
 R = (CH<sub>2</sub>)<sub>n-1</sub>CH<sub>3</sub>

**Table 1** Phase behaviour of bimetallic complexes \*

Complex	M	$n$						
<b>2a</b>	Cu	12	K	$\frac{132.3 (104)}{115.6 (29.5)}$	D <sub>hd</sub>	$\frac{254.4 (1.46)}{249.6 (0.75)}$	I	
			K	$\frac{126.7 (87.4)}{114.1 (24.2)}$		$\frac{232.7 (1.13)}{229.5 (4.97)}$		
		14	K	$\frac{123.5 (115)}{116.0 (34.1)}$	D <sub>hd</sub>	$\frac{219.2 (1.76)}{215.0 (0.42)}$	I	
	<b>3a</b>	Cu	6	K <sub>1</sub>	$\frac{119.2 (2.73)}{99.5 (5.10)}$	K <sub>2</sub>	$\frac{248.5 (3.72)}{243.7 (4.01)}$	I
				K	$\frac{107.8 (268)}{54.6 (279)}$		$\frac{235.7 (5.14)}{232.3 (5.60)}$	
			10	K	$\frac{99.7 (307)}{48.2 (321)}$	D <sub>hd</sub>	$\frac{193.2 (5.56)}{189.5 (5.77)}$	I
12		K	$\frac{90.8 (280)}{40.8 (245)}$	D <sub>hd</sub>	$\frac{169.0 (4.39)}{165.5 (3.59)}$	I		
<b>2b</b>		VO	10	K	$\frac{183.8 (6.14)}{175.1 (6.06)}$	I		
<b>3b</b>	VO	6	K	$\frac{289.9 (38.7)}{267.3 (38.0)}$	I			
		10	K	$\frac{78.5 (51.4)}{48.7 (55.2)}$	D <sub>hd</sub>	$\frac{223.6 (5.14)}{220.6 (4.26)}$	I	
		12	K	$\frac{60.5 (36.4)}{34.2 (38.2)}$	D <sub>hd</sub>	$\frac{187.6 (3.51)}{185.5 (4.85)}$	I	
		14	K	$\frac{48.7 (31.8)}{18.2 (29.9)}$	D <sub>hd</sub>	$\frac{159.5 (0.38)}{156.1 (1.05)}$	I	

\* K<sub>1</sub>, K<sub>2</sub> = crystal phase; D<sub>hd</sub> = discotic hexagonal disordered; I = isotropic; the transition temperature (°C) and enthalpies (in parentheses, kJ mol<sup>-1</sup>) were determined by DSC at a scan rate of 10 °C min<sup>-1</sup>.

**Table 2** Variable-temperature XRD diffraction data for the discotic hexagonal disordered bimetallic complexes **2** and **3**\*

Complex	M	$n$	$T/^\circ\text{C}$	Lattice constant ( $a$ )/Å	$d$ Spacing obs. (calc.)/Å	Miller indices		
<b>2a</b>	Cu	16	170	40.28	34.88 (34.88)	(100)		
					20.14 (20.14)	(110)		
					17.07 (17.44)	(200)		
					5.30 (br)	halo		
					110	46.60	40.35 (40.35)	(100)
							23.29 (23.30)	(110)
		20.16 (20.17)	(200)					
			13.31					
			5.30 (br)		halo			
<b>3a</b>	Cu	12	100	29.66	29.67 (29.67)	(100)		
					14.86 (14.83)	(200)		
					5.04 (br)	halo		
<b>3b</b>	VO	12	100	38.28	33.15 (33.15)	(100)		
					19.13 (19.14)	(110)		
					16.57 (16.58)	(200)		
					4.64 (br)	halo		

\* The measurements were conducted on an INEL MPD-diffractometer with a 2.0 kW Cu-K $\alpha$  X-ray source equipped with an INEL CPS-120 position sensitive detector and a variable-temperature capillary furnace with an accuracy of  $\pm 0.10$  °C in the vicinity of the capillary tube.

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