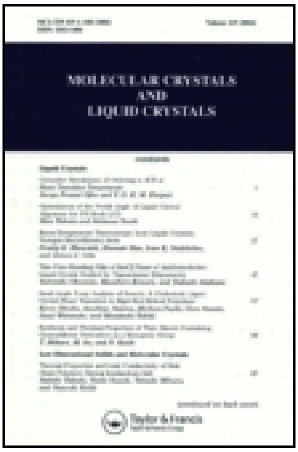

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Effects of Fluoro-Substitution on Mesogenic Properties of Copper and Oxovanadium(IV) Complexes Derived from *β*-(4-Alkoxyphenyl)-Dialdehydes

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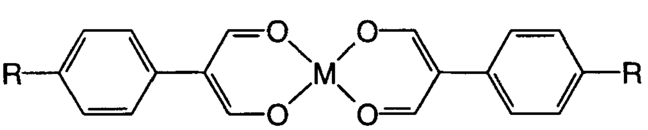
Fluoro-substitution in the phenyl ring of some *β*-(4-alkoxyphenyl)-dialdehydes markedly affects the mesophase behaviour of their copper(II) and oxovanadium(IV) complexes. Fluoro-substitution in the 2-position of the octyl and decyl copper(II) derivatives lowers melting and clearing temperatures, whereas substitution in the 3-position lowers only the former. Fluoro-substitution in the 2-position of the corresponding oxovanadium(IV) complexes usually lowers the melting point, but inhibits mesophase formation.

Keywords: Metallomesogen, fluoro-substitution, copper complexes, oxovanadium(IV) complexes, dialdehyde complexes

1. INTRODUCTION

We recently reported the synthesis of the linear mesogenic complex **1** (R=C_5H_{11}, M=Cu)[1] which has relatively high mesophase transition temperatures (K 220 N 230 I). Increasing the alkyl chain length of R, using alkoxy chains, and changing the metal centre to oxovanadium(IV) all somewhat reduced the mesophase transition temperatures so that for **1** (R=$C_{16}H_{33}O$; M=VO) the transition temperatures are K 170 N 183 I.[2] In organic liquid crystals with phenyl cores, selected lateral substitution in the phenyl rings, especially with fluoro groups, markedly reduces both melting points and mesophase transition temperatures.[3–7] Fluorination of phenyl rings in mesogenic complexes can also be effective, e.g. in copper(II) complexes of *β*-diketones it can lower the melting points dramatically.[8]



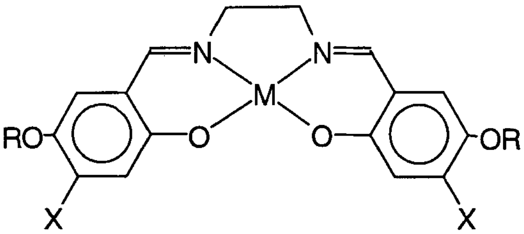
1

TABLE I

Structure of ligands **3** and phase properties of complexes **4**

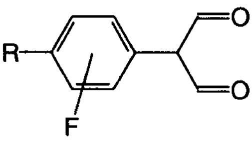
R	Positon of F and ligand number	Phase properties copper complexes	Phase properties oxovanadium(IV) complexes
n-$C_8H_{17}O$	unsubstituted	K 213 N 219 I[(a)]	K 200 I[(a)]
n-$C_8H_{17}O$	2 **(3a)**	K 183 N 187 I **(4a)**	K 170 I **(4b)**
n-$C_8H_{17}O$	3 **(3b)**	K 189 N 221 I **(4c)**	K 235 I (dec) **(4d)**
n-$C_{10}H_{21}O$	unsubstituted	K 207 N 218 I (dec)[(a)]	K 192 N 200 I[(a)]
n-$C_{10}H_{21}O$	2 **(3c)**	K 177 (N 174) I **(4e)**	K 163 I **(4f)**

[(a)] Ref. 2.

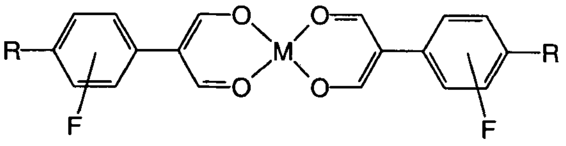


2 (X= F, H; M = Cu, Ni, VO)

Fluorination of mesogenic salicylaldimine derivatives, **2** (X=H), however, lowers clearing temperatures, but discourages mesophase formation.[9] In the hope of further reducing transition temperatures of complexes of type **1**, we have now prepared some fluoro-substituted analogues, **3a–3c**, of the dialdehyde ligand in complex **1**, and report the relationship between phase transition temperatures and structure for their copper(II) and oxovanadium(IV) complexes, **4a–4f** (Table I).



3a -3c



4a, 4c, 4e (M = Cu); 4b, 4d, 4e (M = VO)

2. EXPERIMENTAL

2.1 Preparation of Dialdehydes

2.1.1 *2-Fluoro-4-octyloxyphenylmalonaldehyde* (3a)

This was prepared from 3-fluorophenol by (i) formation of 3-fluoroctyloxybenzene by reaction with octyl bromide in DMF; (ii) Friedel-Crafts acetylation;[10] (iii) conversion of

COMe to CH_2COOH by reaction with thallium nitrate;[11] and (iv) conversion of CH_2COOH to $-CH(CHO)_2$ according to Coppola *et al.*.[12] Recrystallisation from light petroleum (b.p. 60–80°C) gave pale yellow *crystals*, m.p. 68–69°C. (Found: C, 68.7; H, 7.96%. $C_{17}H_{23}FO_3$ requires C, 69.4; H, 7.88%) δ_H($CDCl_3$; $SiMe_4$) 0.9, 1.32, 1.8, 3.92 (3 H, 10 H, 2 H, 2 H; C_8H_{17}), 7.71, 7.11 (2 H, 1 H; C_6H_3), 8.54 (2 H; 2 CH), 14.31 (1 H; OH of enol form).

2.1.2 2-Fluoro-4-decyloxyphenylmalonaldehyde (**3c**)

This was prepared similarly as *crystals*, m.p. 79–81°C. (Found: C, 70.5; H, 8.46%; $C_{19}H_{27}FO_3$ requires C, 70.8; H, 8.44%) δ_H($CDCl_3$; $SiMe_4$) 0.91, 1.34, 1.78, 3.96; (3 H, 14 H, 2 H, 2 H; $C_{10}H_{21}$), 6.72, 7.11 (2 H, 1 H; C_6H_3), 8.53 (2 H; 2 CH), 14.51 (1 H, OH of enol form).

2.1.3 3-Fluoro-4-octyloxyphenylmalonaldehyde (**3b**)

This was prepared similarly as *crystals*, m.p. 75–76°C. Found, C, 69.3; H, 7.93%. $C_{17}H_{23}FO_3$ requires C, 69.4; H, 7.88%). δ_H($CDCl_3$; $SiMe_4$), 0.9, 1.3, 1.84, 4.04 (3 H, 10 H, 2 H, 2 H; C_8H_{17}), 6.95 (3 H; C_6H_3), 8.59 (2 H; 2 CH), 14.23 (1 H; OH of enol form).

2.2 Preparation of Complexes

The complexes were prepared by mixing a warm solution of dialdehyde (0.1 g) in ethanol (2 cm³) with an aqueous solution (1 cm³) containing the requisite amount of copper(II) acetate or oxovanadium(IV) sulphate. They were recrystallised from ethanol. Analytical figures were satisfactory.

C and H Analyses for Complexes

Complex	Formula	%C		%H	
		Found	Calc	Found	Calc
4a	$C_{34}H_{44}CuF_2O_6$	62.7	62.8	6.77	6.82
4b	$C_{34}H_{44}F_2O_7V$	62.3	62.5	6.75	6.78
4c	$C_{34}H_{44}CuF_2O_6$	61.9	62.8	6.73	6.82
4d	$C_{34}H_{44}F_2O_7V$	62.5	62.5	6.86	6.78
4e	$C_{38}H_{52}CuF_2O_6$	64.2	64.6	7.44	7.42
4f	$C_{38}H_{52}F_2O_7V$	64.2	64.3	7.46	7.38

2.2.1 Phase Studies

The phase behaviour of the complexes was examined by using an Olympus BH2 polarizing microscope in conjunction with a Mettler FP5 hot stage and controller.

3. RESULTS AND DISCUSSION

Table I shows the mesophase transition temperatures for the complexes prepared. Only nematic mesophases are seen.

In the copper complexes the presence of 2-fluoro substituents lowers the melting and clearing temperatures by *ca.* 30°C compared with the unsubstituted complex, but does not widen the mesophase. A 3-fluoro-substituent widens the nematic phase considerably by lowering the K-N transition temperature, but does not affect the N-I temperature.

There are bigger differences seen for oxovanadium(IV) complexes. With one exception, these have melting points *ca* 13°C lower than their copper analogues. This has been noted for other series such as unfluorinated dialdehyde complexes,[2] and more markedly, in salicylaldiminato complexes.[13,14] Although often oxovanadium(IV) complexes of a ligand are more mesogenic than the copper complexes, mesophase behaviour in complexes **1** is suppressed or the mesophase temperature range is severely shortened.[2] Further perturbation of the complex from the fluoro-groups in complexes **4** when added to the effect of V=O, then disrupts the packing, enough to curtail any mesophase behaviour.

The subtle effects of fluoro-substitution can also be seen from the way the oxovanadium(IV) complexes **4** of fluorinated ligands **3a–3c** crystallise without water of crystallisation, unlike their unfluorinated analogues.[2] Apparently a single fluoro-substituent is sufficiently hydrophobic to prevent water of crystallisation. Although resulting in changes in the desired direction, lateral fluoro-substitution does not produce dramatic reductions of mesophase transition temperatures. In the copper series lateral fluorination in the 3-position does produce a wider mesophase temperature range, but in the oxovanadium(IV) complexes the balance between producing lowered phase transition temperatures and destroying all mesophase activity is difficult to strike.

Acknowledgements

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