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Criteria for Liquid Crystal Formation in 5-Alkoxy-, 5-Alkylamino-, and 5-Alkanoyl-tropolone Complexes of Transition Metals (Cu^{II}, Zn^{II}, Ni^{II}, Co^{II}, UO$_2^{VI}$, VO^{IV}). The First Uranium Metallomesogen. Crystal Structure of Bis(5-hexadecyloxytropolonato)copper(II)

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The mesophase properties of bis(5-alkoxytropolonato)copper(II) complexes are reported and interpreted in terms of d-layer spacings, which indicate considerable intertwining of the alkyl chains. The mesogenic properties depend on the *nature of the 5-substituent*: to be mesogenic, it must be alkoxy with $n > 8$, and may not be 5-alkanoyl or 5-alkylamino. The *nature of the metal* is also important: to be mesogenic, it may be Cu^{II} or UO$_2^{VI}$ but not Ni^{II}, Zn^{II}, Co^{II}, or VO^{IV}. The crystal structure of bis(5-hexadecyloxytropolonato)copper(II) shows how, even in the crystalline state, molecular packing is dominated by the interactions between alkyl chains, together with copper–oxygen interactions. In the Cu^{II} complexes, strong interactions occur between Cu atoms and O atoms of neighboring molecules. These are stronger than alkyl–alkyl interactions and therefore dominate alkyl–alkyl interactions between neighbors which otherwise govern the possibility and nature of mesogenic properties. The Cu···O interactions disrupt alkyl–alkyl chain interactions enough to produce a mesophase; such interactions do not obtain in the T_d Zn^{II} and Co^{II} complexes, and indeed, these complexes are not mesogenic. Likewise, alkyl chain interactions by the oxygens of the UO$_2^{VI}$ lead to a mesophase, and U constitutes the heaviest metal ever placed into a mesogenic molecule. In the case of VO^{IV}, analogous synthetic steps from VOSO$_4$ led to a new series of binuclear complexes [(VO)$_2$(SO$_4$)(5-alkoxytropoloato)$_2$].

Introduction

Metallomesogens based on Schiff bases use phenyl rings as rigid cores with alkyl chains located opposite but off-center to the metal. We have focused on five- and seven-membered analogues, in which the alkyl chains are opposite, and have formed the first tropolone based metallomesogens.[1,2] Tropolone (2-hydroxycyclohepta-2,4,6-trienone) is a versatile chelating agent, with complexing ability akin to that of β-diketones, (log K_1 for tropolonate−Cu^{2+} is 8.35; for acetylacetonate−Cu^{2+}, it is 8.16). Tropolone cores are of interest as the cores of the natural products hinokitiol (β-thujaplicin, 4-isopropyltropolone), a powerful fungicide, and colchicine which shows strong anti-tumor and anti-gout activity.

Tropolone derivatives have been used as the rigid core of organic mesogens.[3−7] In extending the range of tropolone liquid crystal compounds to include metal complexes, we

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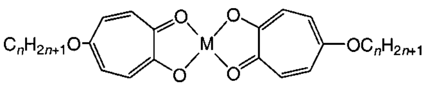
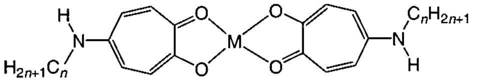
have shown that 5-alkoxytropolone (5-alkoxy-2-hydroxycyclohepta-2,4,6-trienone) complexes **1a**−**e** of copper are metallomesogens.[1,2] This work has been confirmed by Mori.[8,9] Here, we present the *d* spacings in the bis(5-alkoxytropolonato)copper(II) complexes **1b**−**e** from X-ray measurements, which allow interpretation of mesogenic properties in terms of molecular geometry. We further present a basis on which to predict mesogenic properties and synthesize the first uranium metallomesogen. In further support of our results, were able to grow a suitable crystal of the mesogenic bis(5-hexadecyloxytropolonato)copper(II) **1e** and determine its structure.

To verify the criteria for forming mesophases, we have extended the range of metal centers to include zinc(II) (complexes **1f**,**g**), nickel(II) (complexes **1h**−**k**), cobalt(II) (complex **1l**), dioxouranium(VI) (complex **1m**), and oxovanadium(IV) (complexes **1n**,**o**). We also show how changes in the nature of the 5-substituent from 5-alkoxy to 5-alkylamino (complexes **2a**−**d**) and 5-alkanoyl (complexes **3a**−**e**) are reflected in metallomesogen properties.



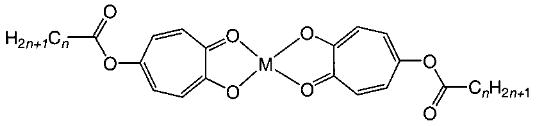
1a - 1p

(1a - 1e, M = Cu; 1f - 1g, M = Zn; 1h - 1k, M = Ni; 1l, M = Co; 1m, M = UO$_2$; 1n - 1p, M = VO)



2a - 2d

(2a - 2c, M = Cu; 2d, M = Ni)



3a - 3e

(3a - 3d, M = Cu; 3e, M = VO)

Experimental

We have described the syntheses of 5-alkoxytropolones by alkylating 5-hydroxytropolone in solvent DMI (1,3-dimethyl-2-imidazolidinone) obviating the need to use HMPA as solvent.[1,2] The complexes of nickel(II), cobalt(II), oxovanadium(IV), and zinc(II) were prepared by refluxing the alkoxytropolone (0.80 mmol), sodium acetate (1.40 mmol), and the metal (as acetate, chloride, or sulfate, 0.44 mmol) in methanol (50 cm^3) followed by cooling in an ice bath. Oxovanadium(IV) and cobalt(II) complexes were prepared under a nitrogen atmosphere in Schlenk glassware. The recrystallization solvent, melting points, and analytical figures are given in Table 1.

Table 1. Bis(5-alkoxytropolonato) Complexes, $(5\text{-}C_nH_{2n+1}O{\cdot}C_7H_4O_2)_2M{\cdot}mH_2O$

no.	*n*	M	mp/°C (recryst solvent)	*m*	%C (theor)	%H (theor)
1a[a]	8	Cu	269[b] (CH_2Cl_2)		64.25 (64.09)	7.58 (7.53)
1b[a]	10	Cu	252[b] (CH_2Cl_2)		65.81 (66.07)	8.34 (8.09)
1c[a]	12	Cu	242[b] (CH_2Cl_2)	2	64.41 (64.24)	8.53 (8.79)
1d[a]	14	Cu	236[b] (CH_2Cl_2)	0.5	68.34 (68.21)	9.26 (9.13)
1e[a]	16	Cu	232[b] (CH_2Cl_2)	0.5	69.70 (69.44)	9.71 (9.50)
1f	10	Zn	194 (MeOH)	0.5	64.71 (64.90)	8.13 (8.17)
1g	12	Zn	188 (MeOH)	1.5	64.61 (64.90)	8.51 (8.74)
1h	10	Ni	197 (EtOH)	1	64.95 (64.67)	8.29 (8.30)
1i	12	Ni	195 (EtOH)	2.5	63.14 (63.39)	8.39 (8.12)
1j	14	Ni	183 (4/1 EtOH/$CHCl_3$)	1	67.53 (67.83)	9.36 (9.22)
1k	16	Ni	172 (4/1 EtOH/$CHCl_3$)		70.51 (70.67)	9.59 (9.54)
1l	14	Co	160 (MeOH)	0.5	68.53 (68.64)	9.37 (9.18)
1m[c]	16	UO_2	207 (EtOH)		55.78 (55.63)	7.57 (7.51)
1n[d]	10	VO	168 (4/1 EtOH/$CHCl_3$)		53.76 (52.04)[e]	6.57 (6.42)
1o[d]	12	VO	161 (2/1 EtOH/$CHCl_3$)		53.92 (54.28)[e]	6.98 (6.95)
1p[d]	14	VO	145 (2/1 EtOH/$CHCl_3$)	1	55.06 (55.14)[e]	7.28 (7.49)

[a] Ref 1. [b] Mesogenic. Clearing point given here. [c] Ref 19. [d] $(VO)_2(SO_4)$(5-alkoxytropoloato)$_2{\cdot}mH_2O$. [e] Analyses %S(theor) **1n** 3.91(4.09), **1o** 3.75(3.81), **1p** 4.11(3.50).

Synthesis of Decylaminotropolone. Sodium hydride in 60% w/w dispersion in mineral oil (1.76 g, 44.00 mmol) was washed with light petroleum (bp 40−60 °C, 2 × 40 cm^3) and then dried under vacuum for 10 min. 5-Aminotropolone (0.6 g, 4.40 mmol) and dry DMI (20 cm^3) were added to the sodium hydride under a stream of nitrogen, and the mixture was stirred at room temperature for 1 h. 1-Bromodecane (1.15 cm^3, 5.20 mmol) was injected into the reaction vessel, and the mixture was stirred for a further 18 h. The solution was filtered, and the green solid collected was washed with light petroleum (bp 40−60 °C, 2 × 10 cm^3) before being suspended in methanol (60 cm^3), with a stream of nitrogen gas blowing over the surface of the solution. Concentrated hydrochloric acid (2 cm^3) was used to acidify the solution to approximately pH 5.0, when a brown suspension was formed. The methanol was then removed using a rotary evaporator to give a dark oil which was cooled over 30 min to give a brown solid. The solid was extracted into dichloromethane (100 cm^3) and washed with water (3 × 100 cm^3) and aqueous saturated sodium chloride (100 cm^3). The dichloromethane layer was dried with calcium chloride before removing the solvent to yield 5-decylaminotropolone (1.01 g, 84%) as an orange powder, mp 110 °C (from cyclohexane). υ_{max}/cm^{-1} (KBr disk): 3290, 3200−2900, 2915vs, 2845vs, 1600, 1440s, 1420s, 1370s, 1210. δ_H(270 MHz; CD_2Cl_2; Me_4Si): 0.85 (3 H, t, *J* 6.9, $-CH_3$), 1.23−1.42 (14 H, m, $(CH_2)_7$), 1.65 (2 H, m, trop−NH−CH_2−CH_2−R), 3.07 (2 H, m, trop−NH−CH_2−R), 6.53 (2H, d, *J* 12.0, trop), 7.20 (2 H, d, *J* 12.0, trop).

5-(Tetradecylamino)tropolone and 5-(hexadecylamino)tropolone were synthesized similarly.

Synthesis of Complexes. Bis(5-decylaminotropolonato)copper(II) 2a. 5-Decylaminotropolone (0.15 g, 0.54 mmol) was added to a hot ethanolic solution (40 cm^3) of copper(II) acetate monohydrate (60 mg, 0.30 mmol) and refluxed for 2 h. The reaction mixture was cooled in an ice bath before a green solid was filtered off. The solid residue was washed with diethyl ether (2 × 20 cm^3), followed by acetone (10 cm^3), before being dried under vacuum for 20 min to yield bis(5-decylaminotropolonato)copper(II) **2a** (0.14 g, 81%) as green platelets, mp 232 °C (from chloroform). (Found: C, 66.35;

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H, 8.41; N, 4.44. $CuC_{34}H_{52}O_4N_2$ requires C, 66.26; H, 8.50; N, 4.55%.) υ_{max}/cm^{-1} (KBr disk): 3500w, 3290w, 2945s, 2891s, 1530s, 1445vs, 1342s, 1286s, 1260s.

5-Alkanoyloxytropolones were made from the reaction of alkanoyl chloride with 5-hydroxytropolone in the presence of a base. Three methods were tried. (a) Alkanoyl chloride with 5-hydroxytropolone and pyridine neat. (b) Alkanoyl chloride and triethylamine in THF. (c) Alkanoyl chloride with 5-hydroxytropolone in the presence of sodium hydride in dry dimethylimidazolidone (DMI) solvent (in preference to HMPA[10]). Yields were in the order (a)/(b)/(c) 31%/42%/57%.

Alkanoylation of 5-Hydroxytropolone Using NaH as Base. 5-Hexadecoyloxytropolone. Sodium hydride in 60% dispersion oil (1.76 g, 44.00 mmol) was washed with light petroleum (bp 40−60 °C, 2 × 40 cm^3) and dried under vacuum for 10 min. 5-Hydroxytropolone (0.6 g, 4.40 mmol) and dry DMI (20 cm^3) were added to the sodium hydride under a stream of nitrogen, and the suspension was stirred at room temperature for 1 h. Hexadecoyl chloride (1.53 cm^3, 5.60 mmol) was injected into the reaction mixture before stirring at 80 °C for 16 h. The solution was cooled and the brown solid filtered off from the black solution. The brown solid was suspended in methanol (30 cm^3) and the resultant suspension acidified carefully with hydrochloric acid (5 cm^3, 0.10 M) to pH 6.8 before adding water (40 cm^3) to precipitate a white solid. The solid was filtered off and extracted into diethyl ether (100 cm^3). The diethyl ether layer was dried with calcium chloride before the solvent was removed. The white solid was washed with a small amount of cold light petroleum (bp 40−60 °C, 10 cm^3) to yield 5-hexadecoyloxytropolone (0.92 g, 57%) as a white powder, mp 106 °C (from hexane). υ_{max}/cm^{-1} (KBr disk): 3200−3000br, 2918vs, 2845s, 1740s, 1600, 1555s, 1460s, 1410s, 1265s. δ_H(270 MHz; CD_2Cl_2; Me_4Si): 0.87 (3 H, t, *J* 7.0, $-CH_3$), 1.22−1.48 (24 H, m, $(CH_2)_{12}$), 1.71 (2 H, m, trop$-CO_2-CH_2-CH_2-$R), 2.53 (2 H, t, *J* 7.0, trop$-CO_2-CH_2-$R), 7.11 (2 H, d, *J* 12.1, trop), 7.26 (2 H, d, *J* 12.1, trop).

5-Octanoyloxytropolone. Pyridine (20 cm^3) as a weak base and solvent, 5-hydroxytropolone (0.30 g, 2.17 mmol), octanoyl chloride (0.35 cm^3, 2.17 mmol), and three drops of DMAP were stirred for 24 h at room temperature to yield, after purification (column chromatography, CH_2Cl_2/AcOEt, 3/1), 5-octanoyloxytropolone (0.18 g, 31%) as colorless crystals, mp 85 °C (from ethyl acetate). υ_{max}/cm^{-1} (KBr disk): 3200−3050br, 2940vs, 2833s, 1740s, 1601s, 1555s, 1460s, 1410s, 1260s. δ_H(270 MHz; CD_2Cl_2; Me_4Si): 0.87 (3 H, t, *J* 7.0, $-CH_3$), 1.25−1.44 (8 H, m, $(CH_2)_4$), 1.73 (2 H, m, trop$-CO_2-CH_2-CH_2-$R), 2.53 (2 H, t, *J* 7.0, trop$-CO_2-CH_2-$R), 7.11 (2 H, d, *J* 12.1, trop), 7.26 (2 H, d, *J* 12.1, trop).

5-Dodecoyloxytropolone. 5-Hydroxytropolone (0.30 g, 2.17 mmol), triethylamine (0.6 cm^3, 4.34 mmol), and dodecoyl chloride (0.46 cm^3) in dry THF (20 cm^3) were stirred for 4 h at toom temperature to yield, after purification (column chromatography as for 5-octanoyloxytropolone), 5-dodecoyloxytropolone (0.29 g, 42%) as colorless crystals, mp 85 °C (from ethyl acetate). υ_{max}/cm^{-1} (KBr disk): 3200−3000br, 2940s, 2833s, 1740s, 1600s, 1555s, 1460s, 1401s, 1260s. δ_H(270 MHz; CD_2Cl_2; Me_4Si): 0.87 (3 H, t, *J* 7.0, $-CH_3$), 1.28−1.44 (16 H, m, $(CH_2)_8$), 1.72 (2 H, m, trop$-CO_2-CH_2-CH_2-$R), 2.53 (2 H, t, *J* 7.0, trop$-CO_2-CH_2-$R), 7.11 (2 H, d, *J* 12.1, trop), 7.26 (2 H, d, *J* 12.1, trop).

5-Octadecoyloxytropolone. This was prepared using octadecoyl chloride (1.60 cm^3, 4.74 mmol) and 5-hydroxytropolone (0.60 g, 4.40 mmol) to yield 5-octadecanoyloxytropolone (0.91 g, 52%) as a white powder, mp 106 °C (from hexane). υ_{max}/cm^{-1} (KBr disk): 3200−3000br, 2918vs, 2845s, 1740s, 1600, 1555s, 1460s, 1410s, 1265s. δ_H(270 MHz; CD_2Cl_2; Me_4Si): 0.87 (3 H, t, *J* 7.0, $-CH_3$), 1.23−1.46 (28 H, m, $(CH_2)_{14}$), 1.71 (2 H, m, trop$-CO_2-CH_2-CH_2-$R), 2.53 (2 H, t, *J* 7.0, trop$-CO_2-CH_2-$R), 7.11 (2 H, d, *J* 12.1, trop), 7.26 (2 H, d, J 12.1, trop).

Metal Complexes of 5-Alkoyloxytropolones. Bis[5-octanoyloxytropolonato]copper(II) 3a. A solution of 5-octanoyloxytropolone (0.20 g, 0.75 mmol) in ethanol (40 cm^3) was stirred at 40 °C while a solution of copper(II) acetate monohydrate (79.6 mg, 0.40 mmol) in ethanol (10 cm^3) was slowly added dropwise into the solution over 10 min. The solution was then refluxed for 1 h before being cooled in an ice bath. A green solid was filtered off and washed with cold acetone (20 cm^3). The solid was purified by Soxhlet extraction with ethyl acetate and solvent removal to yield bis[5-octanoyloxytropolonato]copper(II) **3a** (0.14 g, 72%) as green needles, mp 295 °C (dec) (from ethyl acetate). (Found: C, 61.19; H, 6.47. $CuC_{30}H_{38}O_8$ requires C, 61.05; H, 6.49%.) υ_{max}/cm^{-1} (KBr disk): 2935vs, 2870s, 1810s, 1620w, 1530s, 1445vs, 1360s, 1172s.

Complexes **3b−e** were prepared similarly.

Wide-Angle X-ray Studies. d-Spacings were measured at station 8.2 at Daresbury Laboratory Synchrotron Radiation Source[11,12,13] and evaluated using the computer programs *otoko*[14] and *bsl*.[15]

Crystal Structure Determination. Data for **1e** were collected on the single-crystal diffraction station (no. 9.8) at Daresbury Laboratory Synchrotron Radiation Source.[16,17]

Phase Studies. The phase behavior of the complexes was examined by using an Olympus BH2 polarizing microscope in conjunction with a Mettler FP5 hot stage and controller. Phase transition enthalpies were measured using a Perkin-Elmer DSC-2C with a PC 3600 thermal analysis data station. Heating rates used were normally 10 °C min^{-1}, and the measured onset of the indium standard was 156.66 °C, ΔH 28.50 J g^{-1} (standard[18] value is 156.60 °C, ΔH 28.45 J g^{-1}).

Results and Discussion

Bis(5-alkoxytropolonato) Complexes. Mesogenic Properties. The copper complexes of 5-alkoxytropolones (**1a−e**), although having higher melting points (or higher clearing points for the mesogens) than those of other metals, show mesophases when the alkyl chain length is greater than 8 (Figures 1 and 2, Table 1).[1,2] None of the zinc(II) (**1f**,**g**), nickel(II) (**1h−k**), or cobalt(II) (**1l**) complexes show any mesophases. Although uranyl [dioxouranium(VI)] is similar to oxovanadium(IV) in complexing ability, it is remarkable

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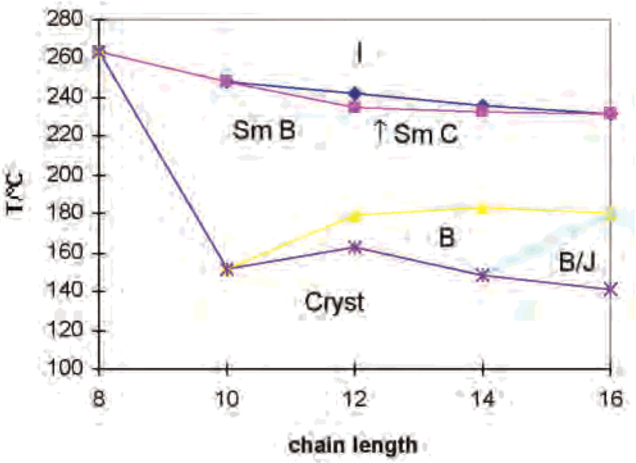

Figure 1. Mesophases of copper tropolonates.

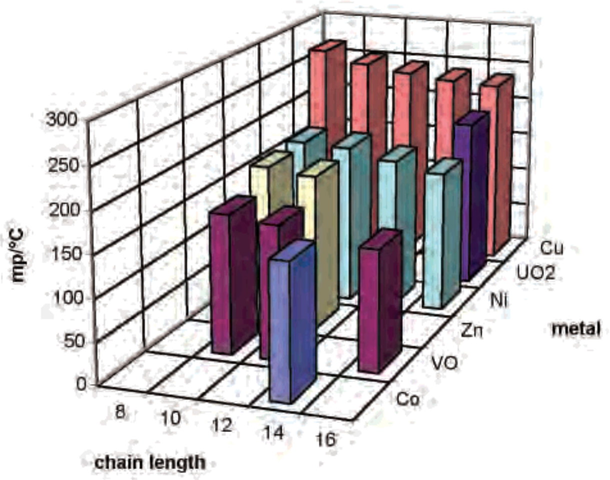

Figure 2. Melting (clearing points) of 5-alkoxytropolate complexes. Variation with the nature of metal core and with alkyl chain length.

that the uranyl complex (**1m**) has a very short temperature range (2 °C) anisotropic plastic liquid crystal phase. A longer chain UO_2 analogue has a wider range but has otherwise similar properties.[19] Here, the two oxo groups of dioxouranium(VI) disrupt the packing of molecules sufficiently for the complex to show a mesophase.

In the Cu^{II} complexes, strong interactions occur between Cu atoms and O atoms of neighboring molecules. These are stronger than alkyl−alkyl interactions and therefore dominate alkyl−alkyl interactions between neighbors which otherwise govern the possibility and nature of mesogenic properties. The Cu···O interactions disrupt alkyl−alkyl chain interactions enough to produce a mesophase. Copper presumably encourages mesophase formation because copper−oxygen interactions disrupt alkyl−alkyl chain interactions enough to produce a mesophase. Square planar complexes of suitable ligands with copper(II) and nickel(II) often give mesogens, where the corresponding tetrahedral complexes of cobalt(II) and zinc(II) are not mesogenic.[20] We attribute this to a disruption of intermolecular interactions, forced by the tetrahedral configuration, sufficient to prevent mesophase formation.

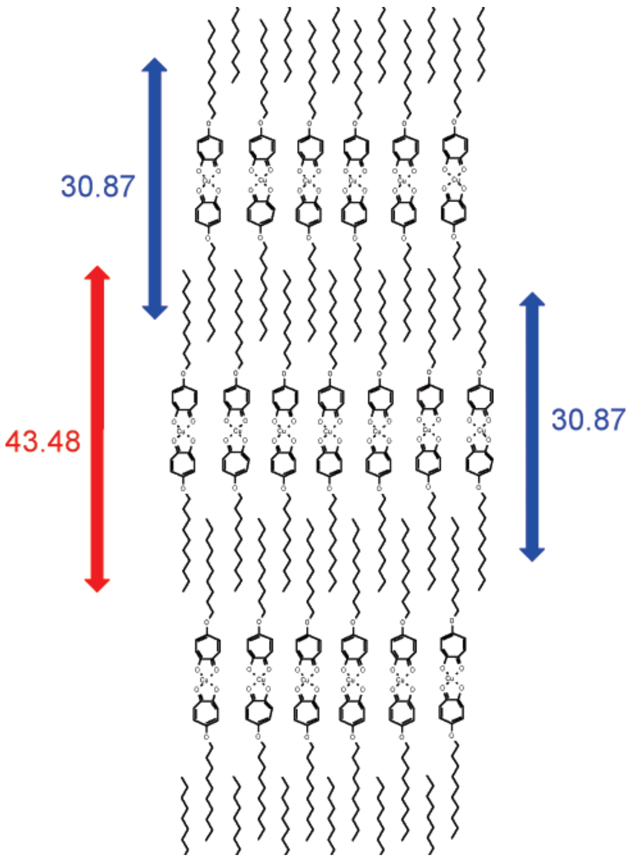

Figure 3. Representation of the layered structure of the S_B phase of bis(5-decyloxytropolonato)copper, **1b**, as indicated by X-ray diffraction data.

Table 2. *d*-Spacing/Å of Bis(5-alkoxytropolonato)Copper Complexes

		d-spacings/Å phase			
cmpd	alkyl chain length *n*	S_B	cryst B	G/J	cryst
1b	10	30.87			21.46
1c	12	22.86	27.55		26.14
1d	14	25.01	30.54		28.94
1e	16	27.33		33.49	31.45

Vanadyl (oxovanadium(IV)) (**1n**−**p**) complexes were prepared similarly to the others. The complexes showed no mesophases. Analysis of these vanadyl complexes showed them to be binuclear and contain sulfate. They analyze as $(VO)_2(SO_4)$(5-alkoxytropolonato)$_2$. Work is continuing on their characterization, but they may be like the sulfato-bridged vanadyl complex reported by Stefan et al.[21]

Bis(5-alkoxytropolonato) Complex d-Layer Spacings. When layer spacing is compared with the known size of a fully extended molecule, it throws light on packing, tilt, and intertwining of external chains. Complex **1b** cools from the isotropic liquid at 248 °C into a S_B phase, with a *d* spacing of 30.87 Å (Table 2). Note the marked difference in *d* spacing in complex **1b** from those of the other complexes. This can be understood in terms of alkyl chain intertwining; the detailed reasoning and discussion follow.

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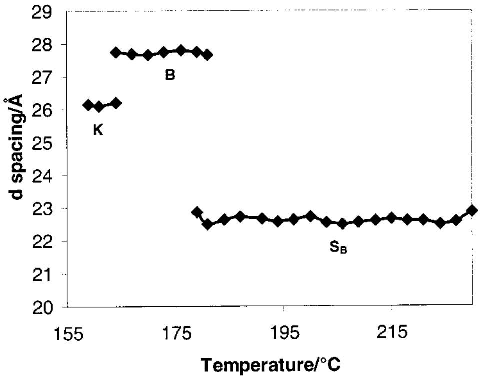

Figure 4. d-Spacing of bis(5-dodecyloxytropolonato)copper **1c** versus temperature (taken as sample cooled).

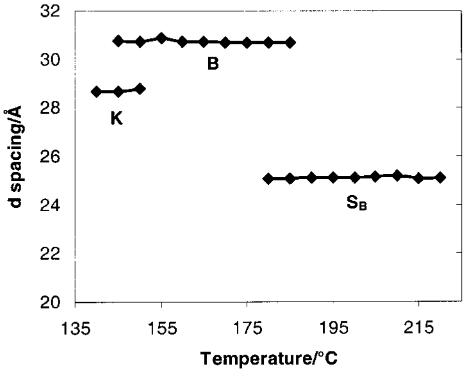

Figure 5. d-Spacing for bis(5-tetradecyloxytropolonato)copper **1d** versus temperature (taken as sample cooled).

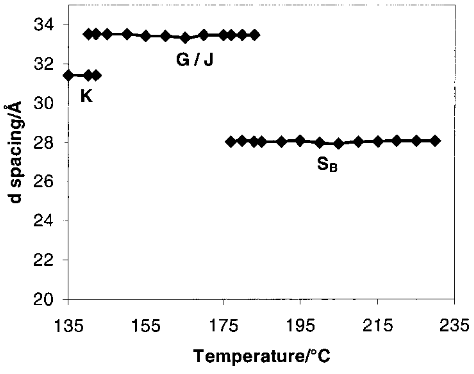

Figure 6. d-Spacing for bis(5-hexadecyloxytropolonato)copper **1e** versus temperature (taken as sample cooled).

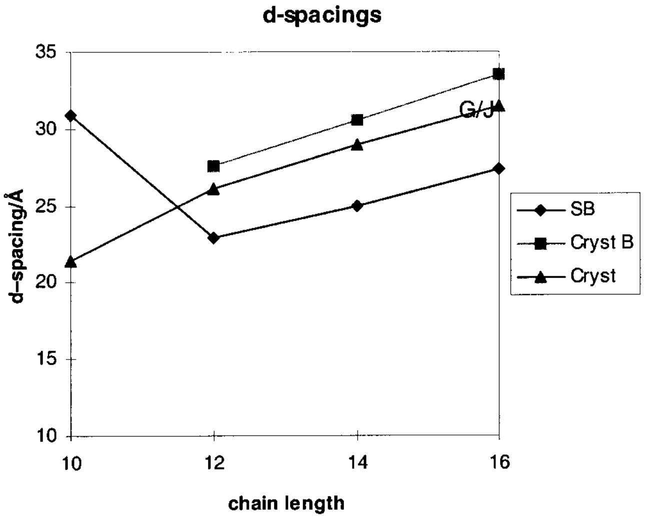

Figure 7. Variation of *d* spacing with chain length.

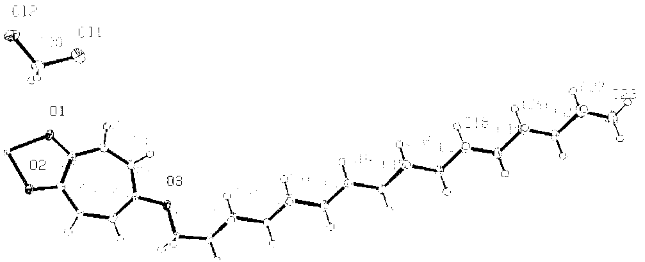

Figure 8. One-half of single molecule of **1e** bis(4-hexadecyloxytropolonato)-copper (repeats through center of inversion at Cu atom).

Table 3. X-ray Crystal Diffraction Data for Bis(5-hexadecyloxytropolonato)Copper Dichloromethane Solvate **1e**·$2CH_2Cl_2$

formula	$CuC_{46}H_{74}O_6 \cdot 2CH_2Cl_2$
mol mass	956.44
syst	triclinic
a, *b*, *c* (Å)	4.1615(8), 9.6687(18), 30.777(6)
α, β, γ **(deg)**	87.414(5), 89.308(5), 81.721(5)
V/Å^3	1224.2(4)
temp/K	150(2)
space group	$P\bar{1}$
Z	1
linear abs coeff, μ	0.710 mm^{-1}
no. reflns measured	7262
no. unique reflns	5728 $R_{int} = 0.0283$
R, wR2 (all data)	0.0792, 0.1553
R, wR2 (2σ data)	0.0588, 0.1437

Starting from the X-ray crystal structure data of **1e**, a truncated molecular model with decyloxy terminal chains (i.e., extended to look like **1b**) gives a length of 43.48 Å for the entire complex. Therefore, the S_B phase of **1b** is formed by the intertwining of terminal alkoxy chains, leading to a layering of the molecules (Figure 3). On cooling below the crystallization temperature at 151 °C, the *d* spacing for **1b** decreases further to 21.46 Å, probably caused by closer packing of the molecules on crystallization to give increased intertwining of the alkoxy chains.

Complex **1c** cools from the isotropic liquid into a S_C phase before transforming to a S_B phase at 235 °C with a *d* spacing of 22.86 Å (Figure 4). Despite the increased length of **1c**, *it shows a decrease* in the layer spacing of the S_B phase when compared to **1b**. This is possibly due to increased intertwining of the alkoxy chains. Further cooling below 179 °C gives an increased *d* spacing of 27.55 Å on formation of the crystal B phase. Finally, crystallization of **1c** at 163 °C gives a minor decrease in the *d* spacing to 26.14 Å, indicating a very small change in the packing of the molecules. This is to be expected, because of the already highly ordered nature of the crystal B phase.

The S_B phase of **1d** is 28.01 Å and is again seen to increase at the transition to the crystal B phase to 30.54 Å. Crystallization at 148 °C reduces the *d* spacing slightly to 28.94 Å (Figure 5).

Complex **1e** has a *d* spacing of 27.33 Å for the S_B phase which increases to 33.49 Å at the transition to the anisotropic plastic crystal phase at 180 °C. Crystallization of **1e** at 141

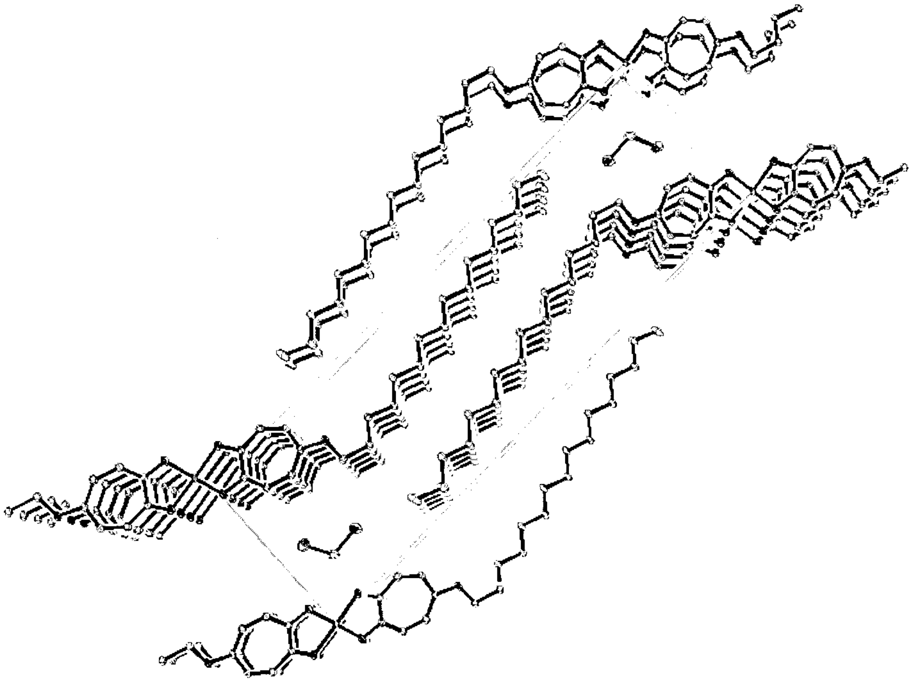

Figure 9. Packing of bis(4-hexadecyloxytropolonato)copper **1e** showing interpenetration of alkyl chains.

°C again gives a small change to the packing of the molecules, with a new layer length of 31.45 Å (Figure 6).

Figure 7 summarizes how *d* spacings change with chain length.

Although aligned samples were not used, *d* spacings from these small-angle X-ray powder studies do confirm the phases assigned by optical microscopy.

Bis(5-alkoxytropolonato) Complexes. Crystal Structures. The crystal structure of **1e** (Table 3, Figure 8) shows the complex adopts a distorted "S" shape. This arises from the eclipsed conformation adopted by the first three carbon atoms of the alkoxy chain. The remainder of the alkyl chain adopts the usual staggered conformation as seen in bis(5-octyloxytropolonato)copper.[1,2] The intermolecular interactions are Cu···Cu, 4.165 Å, and Cu···O (chelating), 3.311 Å. This is quite different from the structure of the nonmesogenic bis(5-octyloxytropolonato)copper which has a Cu···Cu distance of 6.413 Å and a minimum Cu···O (alkoxy) distance of 4.034 Å. The decyloxy derivative shows a smectic B phase when cooling. The hexadecyloxy derivative shows a smectic B phase, then a crystal G/J phase, and the packing in the crystal reflects this (Figure 9). The molecules in the hexadecyloxy derivative are packed about as tightly as those in the octyloxy derivative, although the extra length of the alkyl chains might be expected to lower the density (densities C_8 1.277 g cm^{-3}, C_{16} 1.297 g cm^{-3}). The inclusion of two molecules of dichloromethane along with each molecule of the hexadecyloxy derivative does not significantly alter the density and scarcely affects the packing.

An examination of the carbon bond lengths of the tropolone ring shows only a slight localization of the double bonds. The greatest deviation from mean bond length in the ring is between the two carbons atoms C1 and C7 bonded to the metal chelating oxygen atoms, with a bond length of 1.44 Å. The appropriate accuracy criterion is three times the standard deviation (in this case, 3 × 0.003 Å). Although this limits the discussion of bond localization, the values are significant within experimental error. The crystal structure of unsubstituted bis(tropolonato)copper(II) has been determined three times.[22] Taking the most recent study as the most accurate, the C1−C7 bond is 1.461 Å in bis(tropolonato)-copper(II) and 1.454 Å in tropolone.[23] The average bond length in the tropolone ring is 1.3974 Å. Therefore, the tropolone ring retains a measure of aromaticity in **1e**. The tropolone rings are required by crystallographic symmetry to be parallel to each other and are inclined at 4.6° to the central CuO_4 plane. Selected interatomic distances and angles for **1e** are given in Table 4. Cu−Cu intermolecular separation is 4.162(1) Å. The copper atoms show closer proximity to oxygen (O2) atoms in the form of Cu−O···Cu linkages, with a Cu···O2 intermolecular distance of 3.311(2) Å. Table 5 compares the structures of **1e** with that of bis(5-octyloxytropolonato)copper(II), **1b**. Taking into acccount that the structure of **1b** was determined at room temperature from a rather limited data set, rather than at 150 K, there are no major differences in bond lengths.

Complexes of 5-Alkylaminotropolones (5-Alkylamino-2-hydroxycyclohepta-2,4,6-trienones) and 5-Alkanoyloxytropolones (4-Hydroxy-5-oxo-cyclohepta-1,3,6-trienyl Esters of Alkanoic Acids). In the present series of complexes, the outer arms of the molecules are tropolone−O−alkyl. Attempts were made to extend the range of mesogenic tropolone complexes by linking alkyl groups through other

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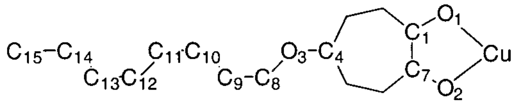
Table 4. Selected Interatomic Distances (Å) and Angles (deg) for **1e**

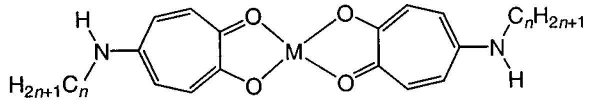
Interatomic Distances			
Cu(1)−O(1a)	1.9036(18)	Cu(1)−O(1)	1.9038(18)
Cu(1)−O(2a)	1.9105(18)	Cu(1)−O(2)	1.9105(18)
O(1)−C(1)	1.297(3)	O(2)−C(7)	1.300(3)
C(1)−C(2)	1.401(3)	C(1)−C(7)	1.440(3)
C(2)−C(3)	1.376(3)	C(3)−C(4)	1.394(3)
C(4)−O(3)	1.371(3)	C(4)−C(5)	1.381(4)
C(5)−C(6)	1.385(3)	C(6)−C(7)	1.403(3)
Intermolecular Distances			
Cu···(2)	3.311(2)(a)	Cu···Cu	4.1615(8)(a)
O(2)···O(2)	3.451(3)(b)	O(1)···O(2)	3.756(3)(a)
Angles			
O(1)−Cu(1)−O(2)	84.45(7)	O(1)−Cu(1)−O(2a)	95.55(7)
C(1)−O(1)−Cu(1)	112.21(15)	C(7)−O(2)−Cu(1)	111.91(15)
O(1)−C(1)−C(2)	118.6(2)	O(1)−C(1)−C(7)	115.7(2)
C(2)−C(1)−C(7)	125.7(2)	C(3)−C(2)−C(1)	131.3(2)
C(2)−C(3)−C(4)	129.6(2)	O(3)−C(4)−C(5)	121.4(2)
O(3)−C(4)−C(3)	111.5(2)	C(5)−C(4)−C(3)	127.0(2)
C(4)−C(5)−C(6)	128.5(2)	C(5)−C(6)−C(7)	131.8(2)
O(2)−C(7)−C(6)	118.3(2)	O(2)−C(7)−C(1)	115.6(2)
C(6)−C(7)−C(1)	126.1(2)	Cl(2)−C(30)−Cl(1)	113.03(17)

Table 5. Comparison of Distances in Bis(5-alkoxytropoloato)-Copper(II) Complexes **1e** (C_{16} Chain) and **1a** (C_8 Chain)



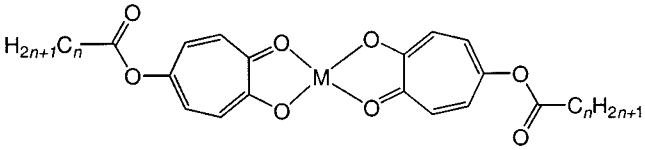
atoms	C16 alkoxy **1e** (Daresbury) distance/Å (−123 °C)	C8 alkoxy **1a**[1] distance/Å (20 °C)
Cu−O(1)	1.904	1.902
Cu−O(2)	1.910	1.916
C(1)−C(7)	1.440	1.43
C(4)−O(3)	1.371	1.49

Table 6. Complexes of 5-Alkylaminotropolones ($(5\text{-}C_nH_{2n+1}NHC_7H_4O_2)_2M\cdot mH_2O$)



cmpd	M	*n*	mp	%C	% (calcd)	%H	%H (calcd)	%N	%N (calcd)	*m*
2a	Cu	10	232	66.35	66.26	8.41	8.50	4.44	4.55	0
2b	Cu	14	223	67.75	67.57	9.41	9.45	3.64	3.75	1
2c	Cu	16	216	68.31	68.08	9.65	9.81	3.35	3.45	1.5
2d	Ni	16	185	69.95	70.04	9.87	9.84	3.41	3.55	0.5

Table 7. Bis[5-alkanoyloxytropolonato] Complexes ($(5\text{-}C_nH_{2n+1}CO_2C_7H_4O_2)_2M\cdot mH_2O$)



cmpd	M	*n*	mp	%C	%C (calcd)	%H	%H (calcd)	*m*
3a	Cu	8	295(d)	61.19	61.05	6.47	6.49	0
3b	Cu	12	292(d)	64.51	64.79	8.20	8.01	0
3c	Cu	16	281	68.06	67.83	8.57	8.66	0
3d	Cu	18	268	67.69	67.57	9.01	9.07	1
3e	VO	18	218	68.65	68.70	9.01	8.97	0

bridging atoms than oxygen. Two series were studied, one with the O atom replaced by NH and the other with the O replaced by C(O)O.

5-Alkylaminotropolones (Table 6) were made by alkylating 5-aminotropolone. Dry dimethylimidazolidone (DMI) was used as a high polarity solvent (in preference to *the hazardous* HMPA used in the literature syntheses[24]) for alkylation with bromoalkanes in the presence of sodium hydride. The complexes prepared are given in Table 6. Neither the copper(II) complexes **2a**−**c** nor the nickel(II) complexes **2d** were mesogenic. The copper derivatives of the 5-alkylaminotropolones showed melting points some 19 °C lower than the clearing temperature of their alkoxy analogues, whereas the nickel(II) derivative melted some 13 °C higher than its alkoxy analogue. The lack of mesophases could be caused by N−H···N hydrogen bonding between adjacent molecules, with a concomitant increase in structural rigidity.

Substitution of an ester link for an ether linkage (Table 7) (alkanoyl derivatives compared with alkoxy) did not produce mesophases even with long C_{16} alkyl chains but did raise melting points of the copper(II) complexes **3a**−**d** by about 35 °C. A similar raising of melting point was found for the oxovanadium(IV) derivative **3e** with a C_{18} alkyl chain. Both the ester and the amino bridges discourage mesophase occurrence in these tropolone complexes.

The structure reported previously was not mesogenic,[2] but the present one is. Chemically, the two differ only in alkyl chain lengths. The crystal structures are also similar for the mesogenic and non-mesogenic analogues. This provides direct evidence for a central theme that one can move smoothly from non-mesogenic to mesogenic with simple chemical modification, in this case a linear alkyl chain length increase.

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Supporting Information Available: Listings of the final values of refined atomic parameters with esd's, bond lengths, and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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