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Lowering Melting Points in Asymmetrically Substituted Salen-Copper(II) Complexes Exhibiting Mesomorphic Behavior. Structure of the Mesogen Cu(5-hexyloxySalen)

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In comparison with their symmetrical analogues, unsymmetrically substituted Cu–Salen complexes show mesophases with lowered melting points. For terminally substituted complexes, symmetrical ones ($R^1 = R^2$) have only an S_A phase, while for unsymmetrical alkoxy substitution a monotropic S_E phase occurs and the melting temperature decreases with no loss in mesophase stability. Lateral substitution, when it is symmetrical ($R^3 = R^4$), lowers mesophase stability but not melting temperature, and when it is unsymmetrical, it greatly lowers both mesophase stability and melting temperature compared with the parent compound. Substitution at the imine carbon (R^5, R^6) also lowers chemical stability (decomposition) of the compounds. The structure of the 5-hexyloxy complex ($R^1 = R^2 = OC_6H_{13}$, $R^3 = R^4 = R^5 = H$) shows the pre-mesophasic arrangement likely adopted after melting.

Introduction

There is great interest in symmetrical and unsymmetrical liquid crystal (or *mesogenic*) compounds,[1] and, because of their ready chemical modifiability, in Schiff base metal complexes.[2–5] The search for applications makes desirable the widest range of ways to modify liquid crystal compounds.[6–10] This leads naturally to unsymmetrical substitution. We have reported symmetrically substituted Salen−copper complexes,[11] particularly the effects of fluoro substitution and substitution of alkyl for alkoxy. These complexes are characterized by high melting and clearing temperatures, whereby detailed investigation is difficult because of decomposition after entering the S_A phase. This work was incomplete in lacking direct structural evidence and the absence of ways to lower the melt temperatures. The high melting points prevented an adequate search for an S_E-S_A phase transition as is observed in the related ($C_n$salen)Ni complexes; notably, this transition is accompanied by a reversible stretching of the interlayer distances.[12]

Here we report a new series of asymmetrically substituted Salen−copper(II) complexes and the crystal structure of a prototype of these complexes[10] as well as ways of decreasing the melting temperatures by lateral and unsymmetrical substitution.

Mesophase stability and melting temperature of nonmetal mesogens can be drastically influenced by unsymmetrical substitution.[1,13] An example is given in Scheme 1.

It is the changes in polarizability and molecular symmetry which lead to the changes in melting and clearing temperatures. From this point of view, the unsymmetrical substitution of the metallomesogens could lower melting temperatures while retaining the mesophase.

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(1) Yelamaggad, C. V.; Hiremath, U. S.; Rao, D. D. S. *Liq. Cryst.* **2001**, *28*, 351.

(2) Hoshino, N. *Coord. Chem. Rev.* **1998**, *174*, 77.

(3) Aiello, I.; Ghedini, M.; La Deda, M.; Pucci, D.; Francesconi, O. *Eur. J. Inorg. Chem.* **1999**, 1367.

(4) Liu, X. H.; Abser, M. N.; Bruce, D. W. *J. Organomet. Chem.* **1998,** *551*, 271.

(5) Demus, D.; Richter, L.; Rürup, C. E.; Sackmann, H.; Schubert, H. *J. Phys. (Paris)* **1975**, *36*, 349.

(6) Chisholm, M. H. *Acc. Chem. Res.* **2000**, *33*, 53.

(7) Kirsch, P.; Bremer, M. *Angew. Chem., Int. Ed. Engl.* **2000**, *39*, 4217.

(8) Bacilieri, A.; Caruso, U.; Panunzi, B.; Roviello, A.; Sirigu, A. *Polymer* **2000**, *41*, 6423.

(9) Weissflog, W.; Lischka, C.; Diele, S.; Pelzl, G.; Wirth, I. *Mol. Cryst. Liq. Cryst.* **1999**, *328*, 101.

(10) Paschke, P.; Zaschke, H.; Mädicke, A.; Chipperfield, J. R.; Blake, A. B.; Nelson, P. G.; Gray, G. W. *Mol. Cryst. Liq. Cryst*. **1988**, *6* (3), 81.

(11) Blake, A. B.; Chipperfield, J. R.; Hussain, W.; Paschke, R.; Sinn, E. *Inorg. Chem*. **1995**, *34*, 1125.

(12) Ohta, K.; Morizumi, Y.; Fujimoto, T.; Yamamoto, I.; Miyamura, K.; Gohshi, Y. *Mol. Cryst. Liq. Cryst.* **1992**, *214*, 161.

(13) Saez, I. M.; Mehl, G. H.; Sinn, E.; Styring, P. *J. Organomet. Chem.* **1998**, *551*, 229.

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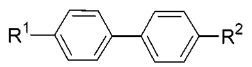
Scheme 1



$R^1 = R^2 = C_6H_{13}$- cr 35°C S_E 35°C S_B 53,5°C I [14]

$R^1 = C_6H_{13}$- $R^2 = C_6H_{13}O$- cr 9°C S_E 68°C S_B 83,9°C I [15]

Substitution around the aromatic rings can promote lower melting points as well as crossover between discotic and calamitic phases,[16,17] which also makes lateral substitutions interesting.

Experimental Section

General. All solvents were purified and dried by standard procedures.[18] C, H, N and Cl, Br analyses were carried out on microanalyzers Carlo Erba 1102 and Leco CHNS-932. ^{1}H NMR spectra were recorded on Bruker WP 200 and Varian Unity 500 with TMS as an internal standard.

The textures and mesophases were studied with an optical microscope "OPTIPHOT-2" (NIKON) equipped with polarized light and a Linkham hotstage TMH 600/S. The hotstage was filled with nitrogen to prevent oxidation. Measurements of transition temperatures were carried out using a Perkin-Elmer DSC-7 calorimeter with a heating or cooling rate of 10 °C/min.

The percentage of copper(II) was determined according a literature method[19] using glycinethymolblue.

The substituted salicylaldehydes **1** and **3** were prepared according to Casiraghi et al.,[20] introducing the formyl group by the paraformaldehyde/tin tetrachloride method.

The symmetrically substituted [Cu(5-hexyloxySalen)]$\cdot$CHCl$_3$ complex was crystallized by slow evaporation of a chloroform solution of [Cu(5-hexyloxySalen)] and characterized by X-ray crystallography.

The preparation of the asymmetric Salen−copper complexes was carried out according to a method of Mandal et al.[21]

Copper(II) Binuclear Complexes 2. To a boiling solution of 0.005 mol of the 5-substituted salicylaldehyde and 0.2 g (0.005 mol) of NaOH in 500 mL of methanol was added a mixture of 2.8 g (0.0075 mol) of $Cu(ClO_4)_2\cdot 6\ H_2O$ and 0.6 g (0.0075 mol) of ethylenediamine, and 10 mL methanol and 10 mL H_2O. The solution was refluxed for 2 h and filtered. The solvent was evaporated until 100 mL was left, the mixture was filtered again, and the solvent was reduced to 50 mL. After crystallization, the product was recrystallized from methanol/H_2O (1:1), yield 15−20%.

Unsymmetrical Substituted *N,N′*-Bis(5-alkylsalicylidene)ethylene-Diaminato-Copper(II) Complexes 4. A 0.0001 mol portion of dimer complex **2** was diluted in 100 mL of methanol. After the addition of 0.0002 mol of substituted salicylaldehyde **3** and 2 drops of triethylamine, the solution was refluxed for 3 h. The solvent was evaporated until 50 mL was left. The precipitate was filtered off and recrystallized from ethyl acetate/toluene, yield 5−10%; satisfactory elemental analyses were obtained.

Table 1

formula, fw	$CuO_4N_2C_{29}Cl_3H_{39}$, 649.5
unit cell lengths *a*, *b*, *c* (Å)	12.126(6), 12.849(5), 11.026(3)
α, β, γ (°); *V* (Å^3)	108.00(2), 102.20(3), 73.86(3); 1559(2)
cell volume	1559(2) Å^3
space group	$P\bar{1}$ (No. 2)
Z	2
D_{calcd}	1.38 g cm^{-3}
μ (Mo Kα)	9.95 cm^{-1}
radiation	Mo Kα (λ = 0.71069 Å)
temp	23 °C
R^a (F_o); R_w (F_o)	0.053; 0.063

[a] $R = \sum\{||F_o| - |F_c||\}/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)]^{1/2} = 0.063$.

X-ray Data Collection and Processing for [Cu(SalenOC$_6$)$\cdot$CHCl$_3$]. A summary of the crystallographic data is given in Table 1. A black fragment crystal of [Cu(SalenOC$_6$)$\cdot$CHCl$_3$], [$CuO_4N_2C_{29}Cl_3H_{39}$], having dimensions 0.25 × 0.25 × 0.70 mm^3, mounted on a glass fiber, was used for unit cell and structure determination. Measurements were carried out as previously described on 3914 reflections of which 2827 were unique ($R_{int} = 0.040$), using the ω-scan method on a Rigaku AFCS diffractometer[22] with graphite monochromated Mo Kα radiation ($2\theta_{max} = 49.1°$; to $h = 10$, $k = 12$, $l = 10$) and were corrected for Lorentz polarization effects and absorption.[23] The intensities of three standard reflections measured after every 150 reflections showed no greater variation than those expected from Poisson statistics. The metal position was determined from a 3-D Patterson function based on all data. This phased the data sufficiently to locate the other atoms from difference Fourier maps. Except for the slightly disordered chlorine atoms of an occluded chloroform molecule, the non-hydrogen atoms were refined anisotropically. The solvent molecule atoms were refined for three cycles and subsequently held fixed. Full-matrix least-squares refinement[24−30] on 1852 reflections with $F_o^2 > 3\sigma(F_o^2)$ (301 variables) gave unweighted and weighted agreement factors of $R = \sum\{||F_o| - |F_c||\}/\sum|F_o| = 0.053$, $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)]^{1/2} = 0.063$. The maximum and minimum shift/error in the final cycle was 0.02 with the highest peak and lowest trough in the final difference map being 0.29, −0.38 e$^-$/Å^3.

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(14) Paschke, R.; Balkow, D.; Baumeister, U.; Hartung, H.; Chipperfield, J. R.; Blake, A. B.; Nelson, P. G.; Gray, G. W. *Mol. Cryst. Liq. Cryst.* **1990**, *188*, 105.

(15) Pura, B.; Rojewska, A.; Zacharski, J.; Przedmojski, J.; Dabrowskli, R. *Liq. Cryst. Conf. Soc. Countries, 4th* **1981**, Abstract A-56.

(16) Elliott, J. M.; Chipperfield, J. R.; Clark, S.; Sinn, E. *Inorg. Chem.* **2001**, *40*, 6390.

(17) Elliott, J. M.; Chipperfield, J. R.; Clark, S.; Sinn, E. *Inorg. Chem. Commun.*, in press.

(18) Perron, D. D.; Armarego, L. F.; *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon Press: New York, 1988.

(19) Pribl, R. *Komplexometrie*; VEB Deutscher Verlag für Grundstoffindustrie: Leipzig, Germany, 1963; Vol. I, p 100.

(20) Casiraghi, G.; Cashati, G.; Puglia, G.; Satori, G.; Terenenghi, G. *J. Chem. Soc., Perkin I* **1982**, 1862.

(21) Mandal, S. K.; Nag, K. *J. Chem. Soc., Dalton Trans.* **1984**, 2839.

(22) Backhouse, J. R.; Lowe, H. M.; Sinn, E.; Suzuki, S.; Woodward, S. *J. Chem. Soc., Dalton Trans.* **1995**, 1489.

(23) An empirical absorption correction, based on azimuthal scans of several reflections, was applied which resulted in transmission factors ranging from 0.78 to 1.22.

(24) Least-squares: function minimized is $\sum w(|F_o| - |F_c|)^2$ where $w = 4F_o^2/\sigma^2(F_o^2)$; $\sigma^2(F_o^2) = [S^2(C + R2B) + (pF_o^2)^2\ ]/Lp^2$; S = scan rate; C = total integrated peak count; R = ratio of scan time to background counting time; p = p-factor; B = total background count; Lp = Lorentz polarization factor.

(25) *TEXSAN-TEXRAY Structure Analysis Package*; Molecular Structure Corporation: The Woodlands, TX, 1985.

(26) The standard deviation of an observation of unit weight $([\sum w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$ where N_o = number of observations, N_v = number of variables) was 2.47.

(27) Neutral atom scattering factors were taken from Cromer and Waber.[28] Anomalous dispersion effects were included in F_{calcd};[29] the values for Δf and $\Delta f'$ were those of Cromer.[30]

(28) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, U.K., 1974; Vol. IV, Table 2.2A.

(29) Ibers, J. A.; Hamilton, W. C. *Acta Crystallogr.* **1964**, *17*, 781.

(30) Cromer, D. T. *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, U.K., 1974; Vol. IV, Table 2.3.1.

Scheme 2

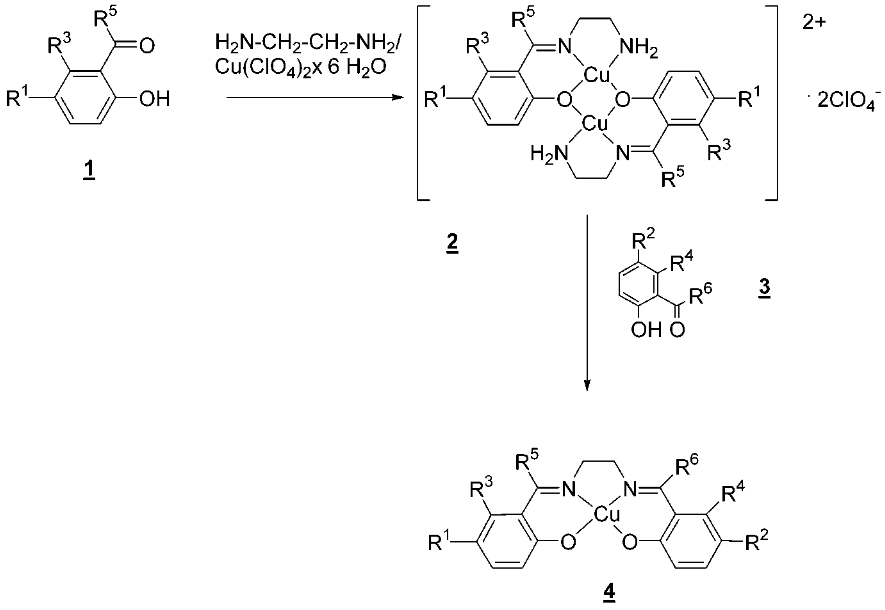
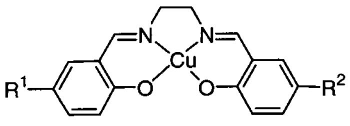


Table 2. Mesomorphic Phase Transition Temperatures (°C) [Enthalpies in kJ mol^{-1}]



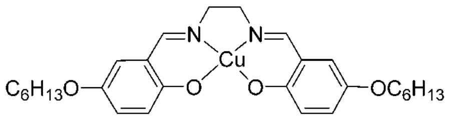
cmpd	R^1	R^2	cryst	S$_E$	S$_A$
4.1	$C_5H_{11}O$	$C_7H_{15}O$	257 [43.9]	(. 165) [6.6]	290 [13.0]
4.2	$C_6H_{13}O$	C_6H_{13}	255		268
4.3	$C_7H_{15}O$	C_5H_{11}	180		210
4.4	$C_7H_{15}O$	C_6H_{13}	195		225
4.5	$C_7H_{15}O$	C_9H_{19}	80.8 [74.5]	226.1 [34.2]	273.1 [12.7]
4.6	C_9H_{19}	C_6H_{13}	215	238	280

Results and Discussion

Synthesis. The typical synthetic procedures are summarized in Scheme 2. The methanolic salicylaldehyde **1** is reacted with a solution of ethylendiamine and cupric perchlorate in methanol/water. The reaction mixture yields either a brown (R^1 = $C_nH_{2n+1}O$—) or green (R^1 = C_nH_{2n+1}—) dimer complex **2**. Attempts to synthesize the corresponding nickel complexes in the same manner failed. Dimer complexes **2** are then reacted with salicylaldehyde **3** in the presence of triethylamine. We presume that the triethylamine forms an intermediate complex by cleaving dimer **2** at the bridging oxygens and coordinating to the copper. Because of the higher stability of chelate complexes, the triethylamine is then replaced by salicylaldehyde **3**. Complexes **4** were obtained in yields of up to 10% and were characterized by elemental analysis.

Mesomorphic Properties. DSC and polarized optical microscopy, under nitrogen atmosphere, were employed to study the phase transition behavior of complexes **4**. The transition temperatures of the asymmetrically terminally substituted copper complexes (**4.1**—**4.6**) are given in Table 2. The high-temperature phase was identified as an S$_A$ phase, and the lower temperature one as an S$_E$ phase, by their characteristic textures (photos have been deposited with the Supporting Information).

The effect of asymmetric substitution is demonstrated by a comparison of Cu(5-hexyloxy)Salen[14] and compounds **4.1** and **4.4**. All these molecules have 14 chain atoms.



Cr 267 S$_A$ 287 I (Lit[10])

1. Cu(5-hexyloxy)Salen exhibits a characteristic high melting temperature. The occurrence of the S$_A$ phase as the only mesophase is typical for all symmetrically substituted Cu—Salen complexes.

2. In case of asymmetrical alkoxy substitution (**4.1**), the mesophase stability is maintained, the melting temperature is decreased, and a monotropic S$_E$ phase occurs.

3. Substitution of one alkoxy chain by an alkyl group (**4.4**) causes a significant decrease in melting but also in clearing temperature.

In addition to the effect of asymmetrical substitution, we studied the effect of lateral substitution, which is also a common way to reduce melting temperatures in ordinary liquid crystal systems (**5.1**, **5.2**, **5.3**, Table 3) and the result of a combination of both effects.

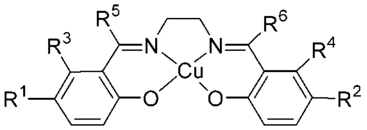
Complexes **5** were prepared according to previous methods,[14] and the unsymmetrical complexes (**4.7**—**4.10**) as described above.

The observed phase transitions lead to the following conclusions:

1. Lateral substitution of a symmetrically substituted metallomesogen causes a loss of mesophase stability but no decrease of the melting temperature (**5.2**/**5.3**).

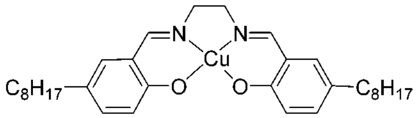
2. Unsymmetrical and lateral substitution leads to a drastic decrease of the mesophase stability and melting temperature.

Table 3. Mesomorphic Phase Transition Temperatures in °C [Enthalpies in kJ mol^{-1}]



cmpd	R^1	R^2	R^3	R^4	R^5	R^6	cryst	S$_A$	N
4.7	$C_7H_{15}O$	C_6H_{13}		CH_3			148		
4.8	$C_7H_{15}O$	C_8H_{17}		CH_3			123 [26.7]		(. 105) [1.2]
4.9	C_8H_{17}	C_8H_{17}			CH_3		229	270	
4.10	$C_8H_{17}O$	C_5H_{11}			CH_3		260 [29.8]	295	
5.1	C_6H_{13}	C_6H_{13}	CH_3	CH_3			294		
5.2	C_8H_{17}	C_8H_{17}	CH_3	CH_3			252		
5.3	C_8H_{17}	C_8H_{17}			CH_3	CH_3	284		

3. The chemical stability of the compounds with methyl substitution in positions R^5 and R^6 is lowered.



Cr 235 S$_A$ 280 I (Lit[10])

Molecular and Extended Structures. Only in the case of the symmetrically substituted Cu(5-hexyloxySalen)•$CHCl_3$ complex were we able to obtain suitable crystals for single-crystal X-ray investigations, by recystallizing Cu(5-hexyloxySalen) from chloroform. Its characterization was effected by the crystal structure determination. Figures 1 and 2 are ORTEP[31] diagrams showing the monomeric fragment and the manner in which these link to form a dimer. Figure 1 shows the atom labeling and the weak interaction between an occluded $CHCl_3$ molecule which hydrogen bonds to the two donor atoms of the salicylaldimine ligand. The chlorine atoms of the occluded solvent molecules show slight positional disorder. The refinement was carried out with and without the disorder, and the two models have little effect on the atomic parameters in the complex molecule. The structure consists of isolated molecules with weak pairwise links (Figure 2) between the Cu atoms and the alkoxy oxygen atoms (Cu•••O = 3.53 Å) of adjacant molecules. The molecular pairs so formed are further linked into pseudo-polymeric chains by weaker (4.01 Å) interactions of the outer alkoxy oxygens with the Cu atoms of adjacant pairs. It is noteworthy that the Cu atoms link to the alkoxy oxygens of the neighboring molecules and not with the salicylaldimine donor atoms,[32] as would be expected in the absence of the alkoxy oxygens. This highlights the difference between alkyl- and alkoxy-substituted complexes, and the differences in behavior between the groups can be understood in terms of this structural difference. These arrangments are expected to be prototypical of these molecules, as is the Cu−Cu distance which is relatively large in this type of dimeric linkage and was found to 6.921(4) Å for this complex.

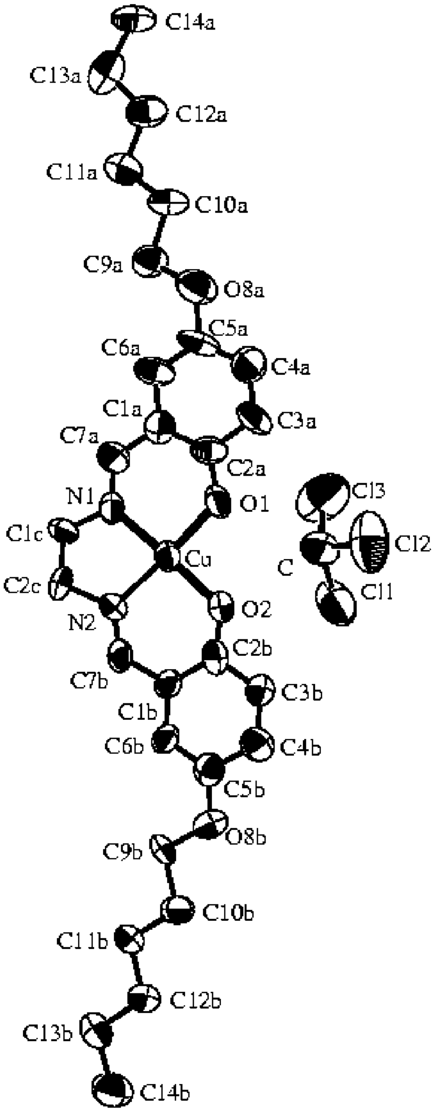


Figure 1. Monomeric unit of the mesogen Cu(5-hexyloxySalen)•$CHCl_3$ showing thermal ellipsoids and atom labeling. H atoms are omitted for clarity.

The occluded $CHCl_3$ is a significant feature in the crystalline form obtained by slow growth from solution but is only of interest as an example of weak hydrogen bonding in a C−H•••O system in the solid state. This occluded $CHCl_3$ is driven off on heating below the melting transition to the mesophase, and as a result, the entire mesogenic behavior occurs in the chloroform-free species. The crystal structure could be determined of the $CHCl_3$ because the $CHCl_3$−Salen donor oxygen atom interaction was strong enough to stabilize the solid at room temperature but not strong enough to keep the chloroform from evaporating at the higher temperatures of the solid−mesogen phase transition.

Conclusions

A significant feature in the crystal structure is that the structure consists of isolated molecules with weakly pairing links, not between the salicylaldimine donor atoms as might

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(31) Johnson, C. K. *ORTEPII*; Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

(32) Sinn, E. Structures and Properties of Homo- and Hetero-Binuclear and Polynuclear Complexes Containing Copper. In *Biological and Inorganic Copper Chemistry*; Karlin, K. D., Zubieta, J., Eds.; Adenine Press: Guilderland, NY 1986.

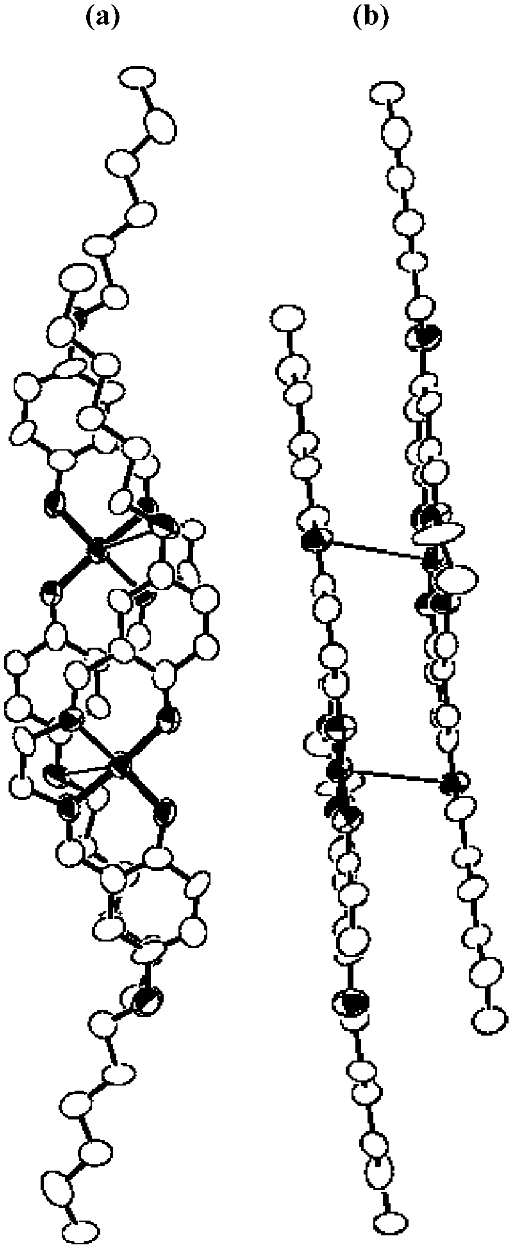

Figure 2. (a) Top and (b) side view of Cu(5-hexyloxySalen), showing the weak dimeric Cu···O linkage involving the olkoxy O atoms. For clarity, C atoms are unshaded and H atoms omitted.

have been expected, but between the Cu atoms and the alkoxy oxygen atoms of adjacant molecules.

This contrasts interestingly with the mesogen bis(5-hexadecyloxytropolonato)copper(II) in which the nearest intermolecular interaction is with the tropolone donor atoms,[33] while an analogue complex, bis(5-octyloxytropolonato)-copper, which does have the nearest Cu···O interaction with a neighboring alkoxy oxygen, is nonmesogenic.[34] It also contrasts with the strong Cu atom to salicylaldimine oxygen bridging for dimer formation when these make the fourth bond to form a dimer between coplanar monomers.[35,36] The occluded $CHCl_3$ in bis(5-hexadecyloxytropolonato)copper(II)·$CHCl_3$ is driven off on heating and has no perceptible effect on the mesogenic properties.

The driving forces toward dimer formation also contrast with those in nickel(II) salicylaldimine complexes: Ni···Ni (*z*-axial) interactions[11] reported in the nickel(II) dimer of *n*-hexyl-substituted Salen, and the unusually strong interactions mediated by both $\pi-\pi$ stacking and CH$-\pi$ interactions discussed by Miyamura et al in the report of the nickel(II) dimer of *n*-butyl-substituted Salen.[37]

We explain the loss of chemical stability with a dimer−monomer transition when the S_A transition is reached. This supports observations by Ohta et al.[12] In the monomer state, the chemical stability at those high temperatures is rapidly decreased, and decomposition takes place.

Asymmetric terminal substitution increases the mesophase range and lowers the melting temperature. The lateral substitution does not have a significant contribution to lowering of the melting temperatures because the central core, and especially the metal center, seems to determine the melting behavior.

Acknowledgment. Support from the EPSRC (UK) is gratefully acknowledged.

Supporting Information Available: Microanalytical data, liquid crystal (S_A, S_A-S_E, and S_E) photomicrographs, and X-ray crystallographic file. This material is available free of charge via the Internet at http://pubs.acs.org.

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(33) Elliott, J. M.; Chipperfield, J. R.; Clark, S.; Teat, S. J.; Sinn, E. *Inorg. Chem.* **2002**, *41*, 293−299.
(34) Chipperfield, J. R.; Clark, S.; Elliott, J.; Sinn, E. *J. Chem. Soc., Chem. Commun.* **1998**, 195−196.
(35) Butcher, R. J.; Sinn, E. *Inorg. Chem.* **1976**, *15*, 1604.
(36) Liebsch, S.; Oakley, M. A.; Paschke, R.; Sinn, E. Submitted for publication.
(37) Miyamura, K.; Mihara, A.; Fujii, T.; Goshi, Y.; Ishii, Y. *J. Am. Chem. Soc.* **1995**, *117*, 2377.