Room-temperature Organometallic Chiral Liquid Crystals: Azoxymercury Complexes

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The new mercury complexes [HgL^{n}Cl] [HL = 4-(n-C_nH_{2n+1})-4′-{S-(+)-2-octyloxy}azobenzene, n = 6,10] are liquid crystals which exhibit a chiral smectic C* mesophase at room temperature and clear at about 60 °C.

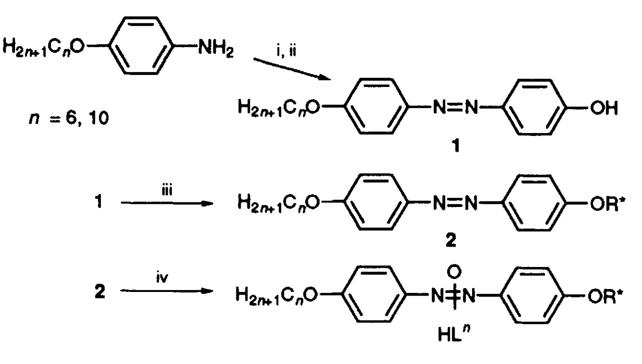
Metallomesogens are liquid crystalline materials with potential applications in optical or electrooptical devices. The basis for this prediction is the physical properties which are assumed to follow from the presence of a metallic centre in a mesogenic molecular skeleton.[1] The synthesis of new mesogenic species, with different ligands, metals or molecule geometries, is therefore currently under way.

Metal-containing compounds which exhibit thermotropic mesomorphism can be either organometallic or coordination complexes. However, while the former species reported up to now are only mercury, palladium or platinum derivatives, the latter ones are more widespread and mesogenic complexes of several transition metals are known.[2–4] Herein, as further examples of organomercury liquid crystals, we report on 4,4′-disubstituted azoxybenzene derivatives.

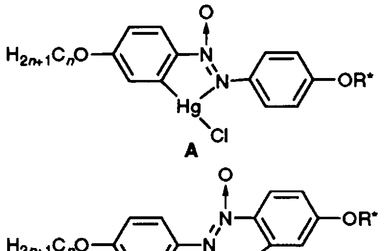
The ligands (HL^n) selected for the present investigation bear in positions 4 and 4′ an aliphatic alkoxy chain, $C_nH_{2n+1}O$ (n = 6, 10), and the chiral S-(+)-2-octyloxy group (R*O), respectively. They were synthesized as shown in Scheme 1 (yields 65–80%) and characterized by elemental analysis, IR, ^1H and ^{13}C NMR spectroscopy.

The mercury complexes [HgL^{n}Cl] (n = 6, 10), were prepared by reacting mercury acetate with HL^n according to the described procedure[6] (yields 40–50%).† Elemental analyses and spectroscopic data (IR, ^1H and ^{13}C NMR) are consistent with 1 : 1 mixtures of the complexes **A** and **B** which are formed by a non-selective metallation of the $C_nH_{2n+1}O$- or R*O-bonded phenyl rings.[7]

In [HgL^{n}Cl], the coordination sphere of the Hg^{II} ion is similar to that for the (2-pyridylphenyl)mercury(II) chloride complex described by Constable *et al.*[8]



Scheme 1 *Reagents and conditions*: i, HCl, $NaNO_2$, in H_2O; ii, PhOH, 2 mol dm^{-3} NaOH in H_2O; iii, R-(−)octan-2-ol according to the procedure described in ref. 5; iv, H_2O_2, AcOH



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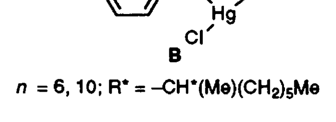


B

n = 6, 10; R* = $-CH^*(Me)(CH_2)_5Me$

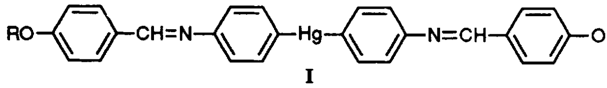
Both the HL^n ligands and their HgCl derivatives are liquid crystals. The mesophases and the transition temperatures are compared in Table 1. In particular, HL^6 shows a cholesteric mesophase in its typical planar oily, streaked texture. This mesophase reflects iridescent light in the visible region of the spectrum. The colour of the reflected light changes from violet to red as the temperature decreases. HL^{10} exhibits a chiral smectic C* phase which appears in its characteristic textures. On heating the crystal, a blurred schlieren SmC* phase is obtained which becomes pseudo-homeotropic when subjected to mechanical stress. Immediately before the SmC*–N* transition, a variant of a marbled texture with typical transition bars is observed. The cholesteric phase exhibits a planar oily, streaked texture. On cooling the isotropic liquid, a fan-shaped cholesteric phase is obtained. The transition to the SmC* phase is characterized by the appearance of various textures in a short range of temperature (schlieren and marbled). The final texture of the SmC* phase is a blurred schlieren with pseudo-homeotropic areas. This mesophase reflects coloured light when subjected to mechanical stress.

With regard to the mercury complexes, both [HgL^{6}Cl] and [HgL^{10}Cl] show an enantiotropic chiral smectic C* mesophase. At room temperature, these complexes show a blurred schlieren SmC* phase. On cooling the isotropic liquid the typical focal-conic fan texture is developed, starting with the

Table 1 Optical and thermal properties of HL^n and [HgL^{n}Cl]

Compound	Transition[a]	T/°C[b]	ΔH/kJ mol^{-1} [c]
HL^6	C–N*	<15.0	
	N*–I	34.0	
	I–N*	33.3	
	N*–C	<15.0	
HL^{10}	C–Sc*	24.5	
	Sc*–N*	36.6	0.1
	N*–I	46.7	1.5
	I–N*	45.6	1.4
	N*–Sc*	35.2	0.1
	Sc*–C	<15.0	
[HgL^{6}Cl]	C–Sc*	<15.0	
	Sc*–I	58.2	3.7
	I–Sc*	56.2	3.6
	Sc*–C	<15.0	
[HgL^{10}Cl]	C–Sc*	<15.0	
	Sc*–I	63.5	9.3
	I–Sc*	58.0	9.1
	Sc*–C	<15.0	

[a] C = Crystal, N* = Cholesteric, S = Smectic; I = Isotropic. [b] Data from optical observations (Zeiss Axioscop polarized microscope equipped with a Linkam CO600 heating stage). [c] Data from DSC (Perkin Elmer DSC-7).



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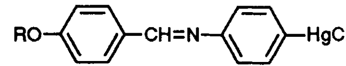

II

formation of 'batônnets.' The pseudo-homeotropic texture is obtained by subjecting the focal-conic texture to mechanical stress.

Liquid crystalline organomercury species **I** and **II** were the first examples of metallomesogens which appeared in the literature. The thermally unstable complexes were described as exhibiting poorly-characterized smectic phases.[9] The new organometallic mercury mesogens described here show a chiral smectic C* phase at room temperature, and therefore extensive investigations into their physical properties, with particular emphasis upon ferroelectricity, are now possible without any restriction due to thermal instability or working temperature.

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Footnote

† The azoxy [HgL^nCl] complexes were obtained in similar yields by oxidation of the corresponding azo-HgCl compounds with hydrogen peroxide.

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