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Metallomesogens with a Manganese Core

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A series of compounds of the formula $[MnCl(L_n)_2]$ (L= N-alkyl[4-(4-decyloxybenzoyloxy)]salicylaldiminato) have been synthesized and their mesomorphic properties studied. These Mn(III) complexes display monotropic nematic phases when the number of carbon atoms of the N-alkyl moiety has from 3 to 9 carbon atoms. Compounds ranging from 5 to 9 carbon atoms also display monotropic smectic C phases. When the N-alkyl part is longer (10 to 16 carbon atoms) only enantiotropic smectic C phases appear. Two complexes were studied by X-ray diffraction showing diffraction patterns that account for the peculiar molecular shape of these molecules.

Keywords: Metallomesogens; manganese; nematic phase; smectic phase; X-ray

INTRODUCTION

The goal of combining liquid crystalline properties and magnetic properties in a material[1] has lead researchers to prepare new metal-containing liquid crystals or metallomesogens.[2] Most of the studies in this field have been focused on paramagnetic nematic liquid crystals, whose director can be oriented parallel or perpendicular to a magnetic field depending on the electronic features of the complex.[3]

We have previously reported that bis{N-alkyl[4-(4-decyloxybenzoyloxy)]salicylaldiminato}copper(II), nickel(II)[4a] or oxovanadium(IV)[4b], and chloro bis{N-4′-alkoxyphenyl[4-(4-decyloxybenzoyloxy)]salicylaldiminato}iron (III)[4c] are new materials which display wide paramagnetic nematic phase ranges.[4] As a continuation of our studies we now report that complexes of the

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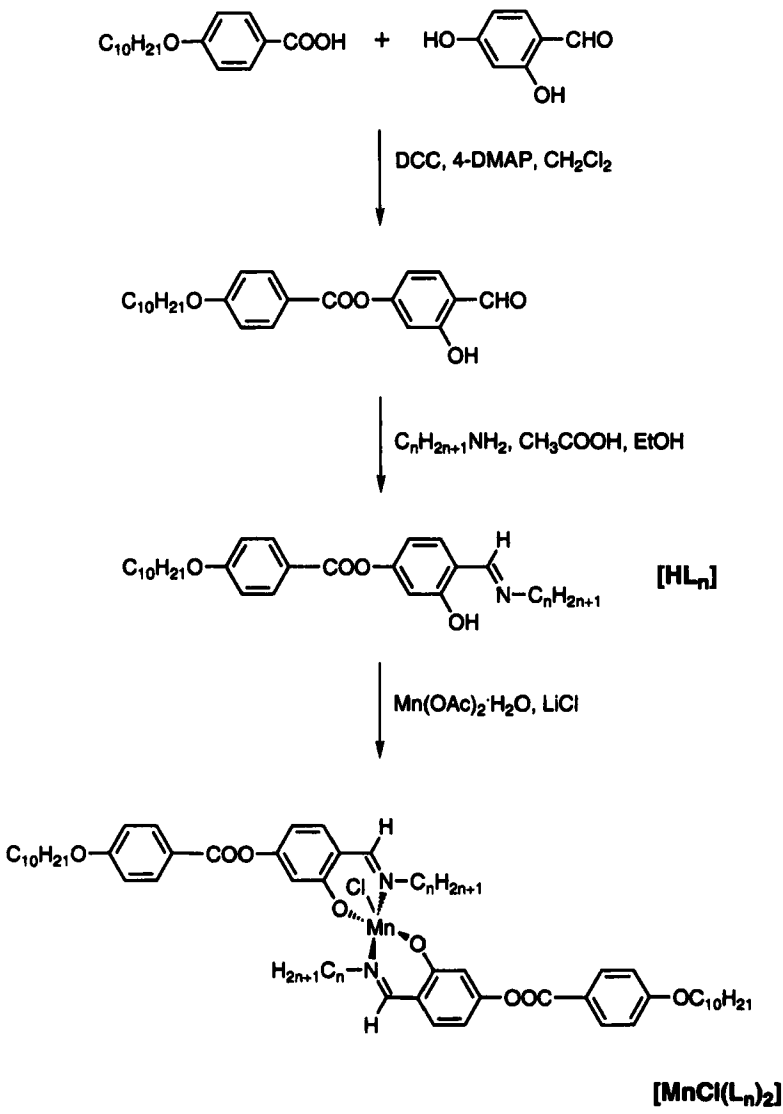

SCHEME 1

formula $[MnCl(L_n)_2]$ (L= N-alkyl[4-(4-decyloxybenzoyloxy)]salicylaldiminato), with the manganese atom in the core, exhibit liquid crystalline properties forming a nematic mesophase and, in some cases, a smectic phase as well.

Only two examples in the literature describe liquid crystalline properties in Mn(III) complexes.[5–6] To our knowledge, these aldimine complexes of manganese(III) are the first mesogenic Mn(III) [N_2O_2] complexes prepared described to date.

We also tried to prepare the N-aryl analogues by several reaction conditions, but we failed, recovering the starting imine in all cases. Perhaps there is steric hindrance around the manganese center. On the other hand, it has been reported for other metals that N-alkyl ligands have more tendency to give nematic phases over a wider range of chain length, and also complexes with these ligands have lower transition temperatures than N-aryl analogues.[4a-b, 7–9]

RESULTS AND DISCUSSIONS

The synthesis of the ligands and the complexes is shown in scheme 1. The Schiff bases were synthesized in two steps following standard procedures. Firstly by reacting 4-decyloxybenzoic acid with 2,4-dihydroxybenzaldehyde using DCC and 4-DMAP in dichloromethane, and secondly by condensation of 4-(4-decyloxybenzoyloxy)-2-hydroxybenzaldehyde with the appropriate alkylamine. The manganese complexes were obtained by heating an ethanolic solution of the imine [HLn] with $Mn(OAc)_2.H_2O$ in the presence of LiCl using a method described in the literature[10]. Both complexes and ligands were satisfactorily characterized by C, H, N microanalysis, mass spectrometry (FAB^+, 3-NBA matrix) and IR spectroscopy (Table I). There is no NMR data for the Mn(III) complexes due to their paramagnetic nature.

The phase behavior and transition temperatures of the ligands and the manganese(III) complexes were studied by optical microscopy and by differential scanning calorimetry (DSC). All these data are gathered in Table II. Some of the ligands have been previously studied in the literature[7a, 8], however we will include these data in order to compare with the transition temperatures of the complexes. All the ligands exhibited liquid crystal properties. Ligands with n=1–6 show an enantiotropic nematic phase (N). Longer aldimines present, in addition to the nematic phase, a smectic C phase (SmC) (monotropic for n=7–9 and enantiotropic for n=10, 12). When n=14, 16 only a smectic C phase appears (Figure 1). The mesophases were identified by optical microscopy.[11] A marbled texture on the heating process and a schlieren texture on cooling allowed us to identify the nematic phase. The smectic C mesophase exhibited a typical blurred texture on heating and a schlieren texture on cooling.

TABLE I Mass spectrometric data, elemental analysis (calculated values in brakets) and IR data for the complexes [MnCn]

n] complexes	*calculated mol. mass*	*FAB$^+$*	*%C*	*%H*	*%N*	*C=Nst (c*
$_4N_2O_8MnCl$	911.4	875 [M-Cl]$^+$	66.1 (65.89)	7.2 (7.03)	2.99 (3.07)	1608
$_2N_2O_8MnCl$	967.5	931 [M-Cl]$^+$	67.4 (67.08)	7.5 (7.51)	2.8 (2.89)	1605
$_6N_2O_8MnCl$	995.6	960 [M-Cl]$^+$	67.3 (67.55)	7.7 (7.63)	2.8 (2.81)	1610
$_0N_2O_8MnCl$	1023.6	988 [M-Cl]$^+$	68.1 (68.06)	8.0 (7.82)	2.7 (2.74)	1606
$_4N_2O_8MnCl$	1051.7	1015 [M-Cl]$^+$	68.7 (68.54)	8.3 (8.00)	2.7 (2.66)	1608
$_8N_2O_8MnCl$	1079.7	1043 [M-Cl]$^+$	69.1 (68.98)	8.4 (8.16)	2.6 (2.59)	1610
$_2N_2O_8MnCl$	1107.8	1072 [M-Cl]$^+$	69.3 (69.38)	8.3 (8.37)	2.4 (2.53)	1610
$_6N_2O_8MnCl$	1135.8	1099 [M-Cl]$^+$	69.9 (69.80)	8.5 (8.46)	2.5 (2.46)	1612
$_0N_2O_8MnCl$	1163.9	1128 [M-Cl]$^+$	70.5 (70.2)	8.6 (8.60)	2.3 (2.40)	1612
$_8N_2O_8MnCl$	1218.5	1183 [M-Cl]$^+$	71.0 (70.9)	8.9 (8.86)	2.3 (2.3)	1610
$_6N_2O_8MnCl$	1276.1	1241 [M-Cl]$^+$	71.7 (71.50)	9.4 (9.10)	2.1 (2.2)	1614
$_4N_2O_8MnCl$	1332.2	1296 [M-Cl]$^+$	71.9 (72.1)	9.5 (9.31)	2.0 (2.10)	1618

TABLE II Optical, thermal and thermodynamic data for the ligands and the complexes

n	*Ligands*			*Complexes*		
	Transition	*Temperature °C*	*ΔH KJ/mol*	*Transition*	*Temperature °C*	*ΔH KJ/mol*
1	C_1-C_2	60.5	2.5	C-I	159.6	53.2
	C_2-N	71.2	31.9	I-SmA[ab]	132.0	
	N-I	95.8	1.1			
3	C-N	68.0	30.9	C-I	136.3	53.0
	N-I	81.9	1.0	I-N[a]	119.8	0.7
4	C-N	61.2	30.3	C-I	135.7	83.6
	N-I	70.7	0.7	I-N[a]	103.6	0.9
5	C-N	68.7	34.4	C-I	106.4	63.1
	N-I	77.5	1.0	C′-I	122.4	1.8
				I-N[a]	105.6	0.9
				N-SmC[a]	49.0	1.3
6	C-N	63.0	31.5	C-I	94.9	50.1
	N-I	73.5	1.2	C′-I	113.8	6.3
				I-N[a]	107.2	0.8
				N-SmC[a]	67.3	2.0
				SmC-S	62.8	
7	C-N	66.7	31.9	C-I	95.7	45.6
	N-I	78.0	1.7	C′-I	113.0	13.4
	N-SmC[a]	51.2	1.2	I-N[a]	112.9	1.9
				N-SmC[ab]	88.4	
8	C-N	65.9	33.6	C-I	100.3	61.2
	N-I	77.0	1.7	C′-I	131.0	9.6
	N-SmC[a]	59.5	1.8	I-N[a]	129.0	0.1
				N-SmC[a]	117.5	1.4
				SmC-S[a]	95.0	0.9
9	C-N	69.7	35.0	C-I	108.8	62.6
	N-I	79.9	2.1	C′-I	122.6	0.9
	N-SmC	66.2[a]	1.8	I-N[a]	121.9	2.0
				N-SmC[ab]	112.1	
10	C-SmC	64.0	35.8	C-SmC	101.0	52.3
	SmC-N	71.4		SmC-I	117.0	1.5
	N-I	78.7	2.2[c]			
12	C-SmC	60.7	34.3	C-SmC	110.4	38.4

n	*Ligands*			*Complexes*		
	Transition	*Temperature °C*	*ΔH KJ/mol*	*Transition*	*Temperature °C*	*ΔH KJ/mol*
	SmC-N	76.3		SmC-I	121.5	1.4
	N-I	79.4	8.1[c]			
14	C-SmC	65.6	38.9	C-SmC	118.5	58.7
	SmC-I	78.9	9.1	SmC-I	132.1	5.4
16	C-SmC	66.6	35.0	C-SmC	116.9	67.2
	SmC-I	79.0	9.1	SmC-I	135.2	1.5

a. Monotropic transition.
b. Optical data.
c. Data corresponding to the sum of two transitions.

The mesophases displayed by the complexes were also identified as nematic and smectic by similar textures to those shown by classical rod-like molecules. The complexes have transition temperatures higher than the ligands (by ca. 40–60°C) (Figure 1). We observe a destabilization of the nematic phase in relation to the corresponding ligands. Now, monotropic nematic phases appear for, and enantiotropic smectic C phases for longer chains n=10–16. Exceptionally, complex with n=1 shows a monotropic smectic A (SmA) identified by its fan-shaped texture. Double melting behavior was observed on the first heating for complexes with n=5–9. On cooling, the mesophases of the complexes with n=1–8 supercool at room temperature and no crystallization peak was observed on the cooling cycle at the DSC termogram. For the complexes with n=3, 4, 5, 6, 8 a cold recrystallization and melting appears in the second heating cycle. This is not the case for the complexes with n= 1 and 7 for which vitrification takes place.

A comparative study of these manganese(III) $[MnCl(L_n)_2]$ compounds and homologous members of copper(II) $[Cu(L_n)_2]$[4a], nickel(II) $[Ni(L_n)_2]$[4a], oxovanadium(IV) $[VO(L_n)_2]$ [4b] series (Table III) allow us to draw some interesting conclusions. Copper and nickel complexes exhibit larger mesogenic temperature ranges than vanadyl and manganese complexes. In general, the temperature range of the mesophase decreases in the order Cu > Ni >VO > Mn. Melting and clearing points are much lower for the manganese complexes compared to nickel and copper ones. An explanation of this phenomenon can be based on the geometries of the ligands around the metal center that are responsible of the planarity of the molecule. The Ni(II) and Cu(II) complexes have approximately a square planar geometry. The oxovanadium(IV) complexes have a square-pyramidal geometry and the manganese core can be described as in the iron complexes[4c] as an intemediate between square-pyramidal (with the chlorine atom in an apical position) and trigonal bipyramidal (with two apical nitrogens).

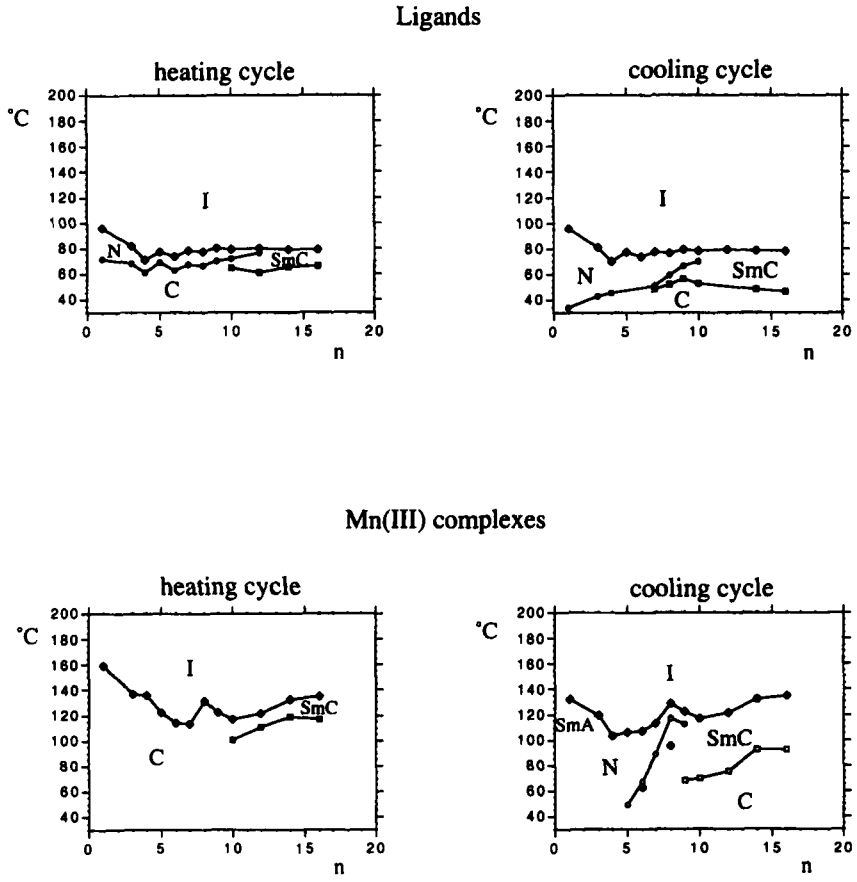

FIGURE 1

Two manganese complexes $[MnCl(L_5)_2]$ and $[MnCl(L_{10})_2]$ were studied in their smectic mesophase by X-ray diffraction. The aim of this study was to confirm the type of mesophase, as well as to determine the structural parameters. The monotropic smectic C mesophase of the compound with n = 5 was obtained by cooling the isotropic liquid through the nematic mesophase. The supercooled smectic mesophase was studied at room temperature in a Pinhole X-ray camera and the diffraction pattern was collected on photographic film. The smectic nature of the mesophase is put into evidence by the presence at low angles of two sharp maxima with a reciprocal spacing ratio 1:2. These maxima are characteristic of lamellar phases and they correspond to the first and second order reflection from the layers. Applying the Bragg's law to these maxima a layer thickness of

30.6 Å is deduced. At high angles, the presence only of a diffuse halo centered at about 4.5 Å is characteristic of the interferences between the conformationally-disordered aliphatic chains. Besides the above mentioned features, commonly found in the diffraction patterns of conventional mesophases, in the X-ray photograph of the mesophase of this compound a diffuse halo is observed at middle angles, that corresponds to an approximate distance of 9.2 Å. This maximum is not observed in classical calamitic liquid crystals, and is probably due to the peculiar geometry of the molecules of this compound. The same phenomenon has been observed before for the nematic and smectic mesophases of some copper(II)[12] and palladium(II)[13] complexes, and it has been accounted for by the existence of short-range side-by-side intermolecular interactions promoted by the peculiar molecular shape. Thus, the experimentally-measured distance of 9.2 Å corresponds roughly to the molecular width. On the other hand, this kind of side-by-side interaction has not been observed in the nematic mesophase of the copper(II), nickel(II) and vanadyl(IV) derivatives of the same ligand[14]. From this one it can be deduced that subtle changes in the molecular architecture, in particular in the coordination geometry of the metal centre, significantly affects the structure of the resulting mesophase.

TABLE III Transition temperatures of homologous metal complexes with the same imine ligand

	$[Cu(L_n)_2]$		$[Ni(L_n)_2]$		$[VO(L_n)_2]$		$[MnCl(L_n)_2]$	
n=1	C-SmC	173.9	C-I	241.5	C-I	157.9	C-I	159.6
	SmC -N	178.2	I-N	213.9			I-SmA	132.0
	N-I	224.0	N-SmC	206.3				
n=5	C-N	104.9	C-N	126.3	C-N	109.4	C-I	122.4
	N-I	146.9	N-I	171.6	N-I	131.0	I-N	105.6
							N-SmC	49.0
n=10	C-N	116.3	C-N	131.9	C-SmC	91.7	C -SmC	101.0
	N-I	134.0	N-I	154.6	SmC-N	103.1	SmC-I	117.0
					N-I	118.4		

The X-ray study of the smectic C mesophase of the manganese complex with n = 10 was performed at 108°C because it recrystallizes easily at room temperature. Only short-exposure photographs could be taken because the samples gradually decompose in the course of the X-ray experiments at high temperatures. For this reason, only a single sharp maximum is observed in the low-angle region, that corresponds to a layer thickness of 35.5 Å. At high angles, the broad halo characteristic of the molten chains is centered at about 4.6 Å. These features

are consistent with the smectic C nature of the mesophase. In this pattern, the above-mentioned middle-angle halo found in the analogous compound with n = 5 is not observed, although this is probably due to the absence of a sufficiently-exposed photograph.

In conclusion, this work shows that smectic liquid crystals stable at relatively low temperatures can be obtained when N-alkyl-[4-(4-decyloxy)benzoyloxy)salilcylaldimines are coordinated to manganese(III). These complexes are good systems on which to carry out physical studies to elucidate their particular properties.

EXPERIMENTAL SECTION

General Methods

Microanalyses were performed with a Perkin-Elmer 240C microanalyser. IR spectra were obtained on a Perkin-Elmer 1600 (FTIR series) spectrometer. Mass spectra were obtained on a VG Autospec EBE (FAB^+, 3-NBA matrix). The optical textures of the mesophases were studied with an Olympus polarizing microscope equipped with a Linkam THMS 600 hot stage, a TMS 91 central processor and a CS196 cooling stage. The transition temperatures were measured by differential scanning calorimetry with a Perkin Elmer DSC-7 operated at a scanning rate of 10°C min^{-1} on heating. The apparatus was calibrated with indium (156.6°C, 28.4 J g^{-1}) and tin (232.1°C, 60.5 J/g) as standards. X-ray diffraction patterns were obtained using a Pinhole camera (Anton-Paar) operating with a point-focused Ni-filtered Cu Kα beam.

The sample was held in Lindemann glass capillaries (1 mm diameter) and heated with a variable-temperature attachment. The diffraction pattern was collected on flat photographic film.

Synthesis of the 4-(4′-decyloxybenzoyloxy)-2-hydroxybenzaldehyde

To a solution of 20 mmol (5.56 g) of 4-decyloxybenzoic acid and 20 mmol (2.76 g) of 2,4-dihydroxybenzaldehyde in 100 mL of dry dichloromethane are added 20 mmol (4.13 g) of dicyclohexylcarbodiimide (DCC) and 2 mmol of 4-N,N-diaminopyridine (DMAP). The mixture is stirred at room temperature for 2 hours. Afterwards, the urea formed is filtered off and the solvent evaporated. Column chromatography (eluent: hexane/ethyl acetate 98/2) of the residue yields 4 g (50%) of the product in pure form. IR (cm^{-1}): 1734 (COO), 1653 (CHO),

1253 (CO). ^{1}H NMR (300 MHz, $CDCl_3$, ∂ ppm): 0.84–0.89 (m, 3H), 1.26, 1.81 (m, 16H), 4.03 (t, J= 6.6 Hz, 2H), 6.85 (d, J = 2 Hz, 1H), 6.9 (dd, J= 2 Hz, J = 8.5 Hz, 1H), 6.95 (d, J = 8.8 Hz, 2H), 7.6 (d, J = 8.5 Hz, 1H), 8.1 (d, J= 8.8 Hz, 2H), 9.8 (s, 1H), 11.2 (s, 1H).

General procedure for the preparation of the imines [HL_n]

A solution of 1.25 mmol (0.5 g) of the 4-(4'-decyloxybenzoyloxy)-2-hydroxybenzaldehyde and 1.25 mmol of the appropriate alkylamine in absolute ethanol, and 3 drops of acetic acid are refluxed for 2 hours. After cooling, the precipitate is filtered and recrystallized in absolute ethanol. Characterization data for [HL_{10}]: IR (cm^{-1}): 1714 (COO), 1626 (CN), 1253 (CO). ^{1}H NMR (300 MHz, $CDCl_3$, ∂ ppm): 0.84–0.88 (m, 6H), 1.2–1.8 (m, 32H), 3.6 (t, J = 6.6 Hz, 2H), 4.0 (t, J= 6.6 Hz, 2H), 6.7 (dd, J= 2.2 Hz, J = 8.3 Hz, 1H), 6.8 (d, J = 2.1 Hz, 1H), 6.9 (d, J = 8.8 Hz, 2H), 7.2 (d, J = 8.4 Hz, 1H), 8.1 (d, J = 8.8 Hz, 2H), 8.3 (s, 1H), 14.1 (s, 1H).

General procedure for the preparation of the Mn(III) complexes is as follows

To 1 mmol of the corresponding imine dissolved in 20 ml of absolute ethanol are added 0.5 mmol of $Mn(OAc)_2.H_2O$. The mixture is refluxed for 2 hours. Then, 3 mmol of LiCl are added and the mixture refluxed for 1 hour. After cooling at 0°C, the complex precipitates as black brown crystals that are filtered, washed with water and vacuum dried. Characterization data are shown on Table I.

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