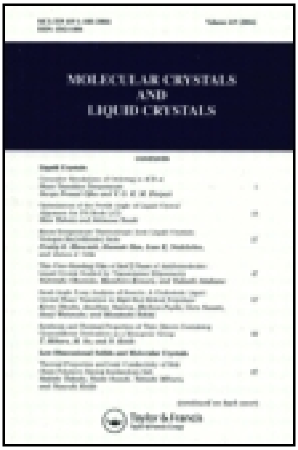

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Mesogenic Properties of Nickel(II) Complexes of N-(2-hydroxy-4-n-alkyloxybenzylidene)4″-n-dodecylphenylanilines

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Mesogenic Properties of Nickel(II) Complexes of *N*-(2-hydroxy-4-*n*-alkyloxybenzylidene)4″-*n*-dodecylphenylanilines†

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Continuing our efforts to synthesise metallomesogens to study the influence of different transition metals on the mesophases, a series of nickel(II) complexes of *N*-(2-hydroxy-4-*n*-alkyloxybenzylidene)-4″-*n*-dodecylphenylanilines have been prepared. These predominantly exhibit smectic A and smectic C phases. A comparison of the mesomorphic behaviour of these complexes with those of the corresponding copper(II) and palladium(II) complexes has been made. It was found that the palladium complexes have the highest thermal stability of the mesophase while the nickel complexes have the lowest melting points. Preliminary experiments on magnetic measurements have shown that these nickel complexes are diamagnetic in the solid state and exhibit paramagnetic properties in chloroform solution.

Keywords: nickel(II) complexes, smectic A, smectic C

INTRODUCTION

The interest in the synthesis and properties of metallomesogens has grown particularly over the last few years.[1] Of the several transition metals that can be used in the synthesis of metallomesogens, copper(II) and palladium(II) have been utilised widely.[1] The mesogenic tetra coordinate complexes of these are square-planar; while the copper complexes are all paramagnetic, the palladium complexes are diamagnetic without exception. A variety of mesophases have been obtained using these metal ions. However, the influence of the different metals on either the nature of the mesophase or the transition temperatures is not clear. For example, copper(II) and palladium(II) complexes of *N*-(4-(4′-*n*-alkyloxybenzoyloxy) salicylidene)-4-*n*-butylaniline show mesomorphic properties while the corresponding nickel(II) complexes are non-mesomorphic.[2] In fact, there are very few mesogenic salicylaldimine nickel complexes that have been reported so far.[3–5] We have recently reported[6] two homologous series of copper and palladium complexes using

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salicylaldimines as ligands which exhibit mesomorphic properties. In continuing our effort to understand the influence of the metal on the mesophase, a homologous series of nickel(II) complexes of structure A has been prepared and their mesogenic properties are discussed here.

A comparison of the mesomorphic properties of these nickel(II) complexes with those of the corresponding copper(II) and palladium(II) complexes[6] has been made. Also, the other reported nickel complexes of salicylaldimines have been considered for discussion. In general, nickel complexes show rather interesting magnetic behaviour depending on whether they have square planar or tetrahedral configuration. The complexes under discussion here are diamagnetic in the solid state and are paramagnetic in chloroform solution.

EXPERIMENTAL

The Schiff's bases (ligands) were synthesised according to a procedure described by us previously[6] and all of them are mesogenic. All the nickel(II) complexes (A) were prepared by a general method and is described below for the pentyloxy (n = 5) derivative.

Bis[*N*-(4″-*n*-dodecylbiphenyl)-4-*n*-pentyloxysalicylaldiminato]nickel(II)

A mixture of *N*-[2-hydroxy-4-*n*-pentyloxybenzylidene)-4″-*n*-dodecylphenylaniline (1.06 g, 0.002 mol), nickel(II) acetate tetrahydrate (0.25 g, 0.001 mol), potassium carbonate (0.41 g, 0.003 mol) and acetonitrile (50 ml) was stirred and heated at 60°C for eighteen hours. The mixture was cooled and filtered. The dark solid material was taken up in chloroform (100 ml), washed with water (3 × 30 ml) and dried (Na_2SO_4). Removal of solvent and crystallisation of the residue from butan-2-one afforded dark green crystals. Yield 0.8 g, 72%; m.p. 152°C; IR(Nujol) ν_{max}: 1595 and 1610 cm^{-1}; UV-Vis $\lambda_{max}^{CHCl_3}(\varepsilon)$: 352 (30,200) 277(50,600) 258(45,400) 226(42,500).

Anal. calcd. for $C_{72}H_{96}O_4N_2Ni$: C, 77.98; H, 8.64; N, 2.52%.
Found: C, 78.12; H, 8.34; N, 2.63%.

The yields and the microanalytical (Carlo-Erba 1106) data obtained for the remaining complexes are reported in Table I. Further, all the ligands and complexes have been characterised by infrared spectroscopy (Shimadzu-IR435) as Nujol mull, electronic absorption spectroscopy (Hitachi U-3200) in chloroform solution and NMR spectroscopy (Bruker WP80SY FT-NMR) in deuterochloroform with tetramethylsilane as an internal standard. The phase behaviour of all complexes were observed with a polarising microscope (Leitz Laborlux 12 POL) equipped with a heating stage (Mettler FP52 and FP5). A differential scanning calorimeter (Perkin-Elmer DSC-4) was also used for this purpose as well as for determining the enthalpies of transitions. The calorimeter was calibrated using pure indium as a standard and a heating and cooling rate of 5°C/min was employed. The magnetic measurements were carried out on a Lewis coil force magnetometer (George Associates, Model 300).

TABLE I

Elemental analysis data of bis[*N*-(4″-*n*-dodecylbiphenyl)-4-*n*-alkyloxysalicylaldiminato]nickel(II), A

n	Molecular Formula	Yield[a] %	Elemental analysis % (calc.)		
			C	H	N
1	$C_{64}H_{80}O_4N_2Ni$	58	77.25(76.89)	8.26(8.01)	2.66(2.80)
2	$C_{66}H_{84}O_4N_2Ni$	49	77.68(77.14)	8.29(8.18)	2.58(2.72)
3	$C_{68}H_{88}O_4N_2Ni$	38	77.66(77.36)	8.60(8.34)	2.25(2.65)
4	$C_{70}H_{92}O_4N_2Ni$	64	77.51(77.58)	8.66(8.49)	2.56(2.58)
6	$C_{74}H_{100}O_4N_2Ni$	40	77.96(77.98)	9.13(8.78)	2.16(2.45)
7	$C_{76}H_{104}O_4N_2Ni$	44	78.49(78.16)	9.10(8.91)	2.04(2.39)
8	$C_{78}H_{108}O_4N_2Ni$	42	78.05(78.34)	9.17(9.03)	2.30(2.34)
9	$C_{80}H_{112}O_4N_2Ni$	37	78.70(78.51)	8.96(9.16)	2.16(2.29)
10	$C_{82}H_{116}O_4N_2Ni$	32	78.49(78.67)	8.94(9.27)	2.34(2.23)
11	$C_{84}H_{120}O_4N_2Ni$	34	78.45(78.83)	9.59(9.38)	2.08(2.18)
12	$C_{86}H_{124}O_4N_2Ni$	38	79.12(78.97)	9.89(9.48)	1.79(2.10)
18	$C_{98}H_{148}O_4N_2Ni$	49	79.51(79.74)	10.40(10.03)	1.76(1.89)

[a] The yields reported above are for analytically pure compounds.

RESULTS AND DISCUSSION

The transition temperatures and enthalpies determined for the bis[*N*-(4″-*n*-dodecylbiphenyl)-4-*n*-alkyloxysalicylaldiminato]nickel(II) complexes are reported in Table II. As has been found in a large number of metallomesogens, these complexes also invariably exhibit crystal-crystal transitions. All the homologues are enantiotropic smectic. For homologues (*n* = 1–4), only a smectic A phase with characteristic focal-conic texture was seen. The next five homologues (*n* = 5–9) exhibit in addition to a smectic A phase, a smectic C phase with broken focal-conic texture. The typical photomicrographs of the texture exhibited by these are shown in Figure 1a and b respectively. The remaining homologues (*n* = 10–12, 18) exhibit only a smectic C phase. All these complexes have fairly wide mesophase ranges; for example, complex A, *n* = 2 has a smectic A range of 124.5°. The nickel complexes are thermally stable over the temperature range of the mesophase. None of these decompose at their clearing points and the transition temperatures are reproducible after several heating and cooling cycles.

Two homologous series of similar copper(II) and palladium(II) complexes reported[6] by us earlier also show enantiotropic smectic A and smectic C phases. However, in the present series of complexes smectic A phase is not observed for homologue with

TABLE II

Transition temperatures (°C) and enthalpies (kcal/mol) of bis[*N*-(4″-*n*-dodecylbiphenyl) 4-*n*-pentyloxysalicylaldiminato nickel(II), A

Compound No.	n	C_2		C_1		C		S_C		S_A		I
1	1	-		.	119.0 5.09	.	158.5 9.57	-		.	240.5 3.0	.
2	2	.	88.5 11.24	.	122.0 4.98	.	144.5 3.18	-		.	269.0 4.34	.
3	3	.	89.5 5.37	.	108.0 10.5	.	161.5 2.14	-		.	261.0 4.32	.
4	4	.	69.0 2.55	.	94.5 8.15	.	157.5 2.46	-		.	262.5 3.89	.
5	5	-		.	96.0 10.51	.	152.0 0.55	.	168.5*	.	245.5 3.80	.
6	6	-		.	90.0 9.38	.	160.0 1.38	.	199.0*	.	243.5 4.03	.
7	7	.	85.0 1.78	.	114.5 1.34	.	176.5 3.53	.	214.0*	.	240.5 3.05	.
8	8	.	126.5 0.28	.	151.5 1.64	.	180.0 4.83	.	222.0*	.	237.0 3.66	.
9	9	.	74.0 1.49	.	95.0 2.78	.	156.5 3.99	.	220.5*	.	227.5 3.26	.
10	10	.	59.5 0.71	.	106.5 5.46	.	157.0 2.80	.	220.0 4.01	-		.
11	11	.	81.0 5.30	.	109.0 3.91	.	140.0 4.45	.	210.0 4.30	-		.
12	12	.	70.0 6.54	.	114.5 2.63	.	141.0 3.95	.	196.5 3.12	-		.
13	18	-		.	79.0 12.63	.	122.5 1.03	.	179.0 4.18	-		.

C_2, C_1 & C : crystalline phases; S_C : smectic C phase; S_A : smectic A phase;

I : isotropic phase.

*The enthalpies could not be determined.

n = 10 and onwards. The enthalpies of smectic A—isotropic transition of the nickel complexes are relatively higher, viz., about 3 to 4 kcal/mol.

A plot of the phase transition temperatures as a function of the number of carbon atoms in the alkyloxy chain of the nickel complexes, A, is given in Figure 2. As can be seen the behaviour is similar to what has been observed for a number of series of calamitic mesogens. There is alternation for the smectic A—isotropic transition up to the pentyloxy derivative beyond which there is a con-

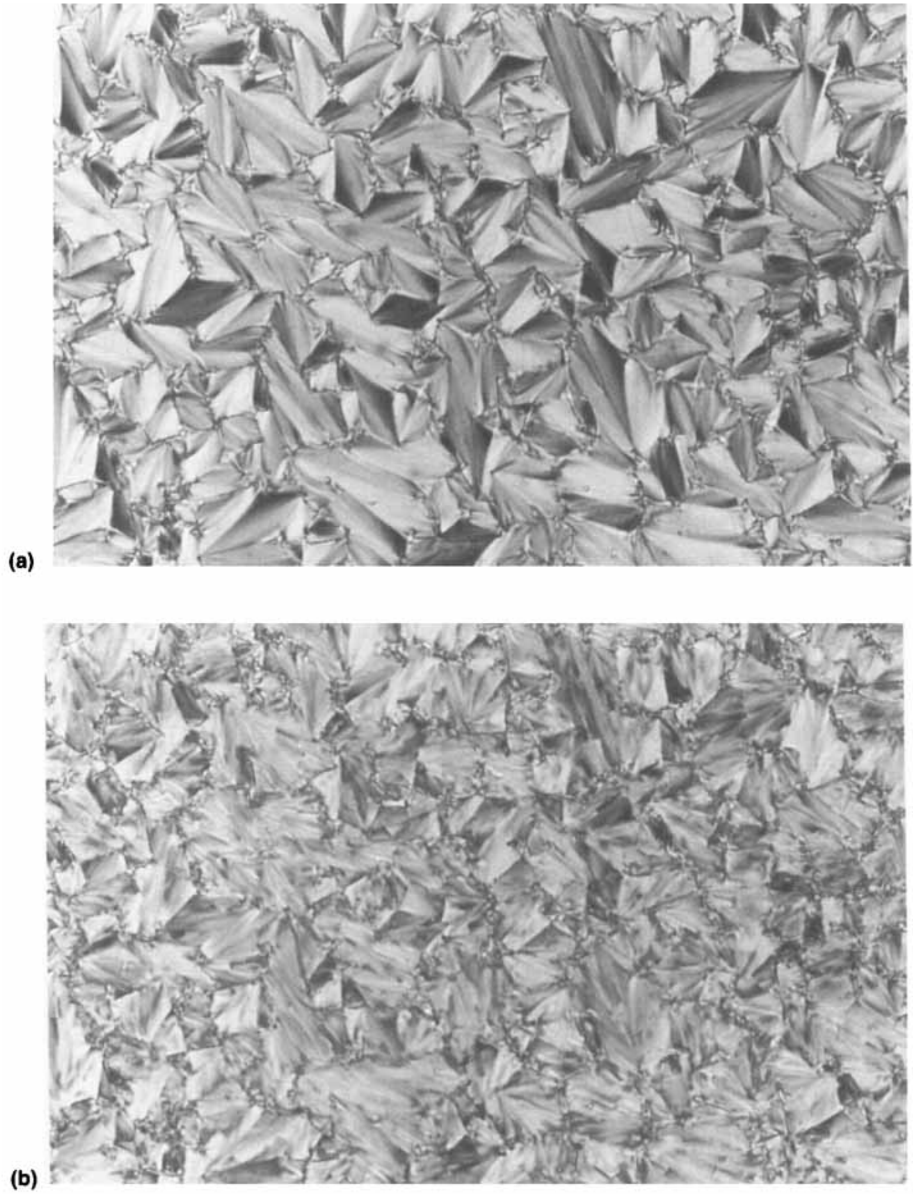
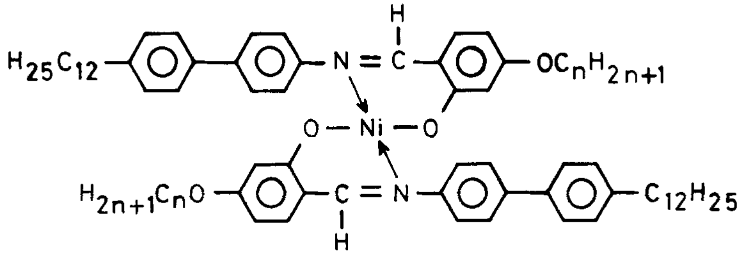


FIGURE 1 Microscopic texture observed on cooling the isotropic liquid of complex (A), $n = 8$. (a) Focal-conic texture of the smectic A phase at 225.0°C, Magnification ×80. (b) Broken focal-conic texture of the smectic C phase (same region as a) at 218.0°C, Magnification ×80. See Color Plate X.

tinuous decrease. Similarly, the smectic C-smectic A transition points follow a smooth curve.

Though there are only very few homologous series of nickel complexes that have been reported so far, their behaviour is quite contrasting. For example, a series of bis[4-{(4-*n*-decyloxybenzoyl)oxy}-*N*-*n*-alkylsalicylaldiminato]nickel(II)

A



complexes[7] and a series of bis[4-((4-*n*-alkyloxybenzoyl)oxy)-*N*-*n*-propylsalicylaldiminato]nickel(II) complexes[5] exhibit a nematic phase while the entire series of bis[*N*-(4-*n*-butylphenyl)-4″-*n*-alkyloxybenzoyloxysalicylaldiminato]nickel(II) complexes are non-mesomorphic. The absence of mesomorphism in the latter series of complexes has been attributed to the non-planar configuration of the chelate rings. However, a comparative study of some mesogenic copper, nickel and oxovanadium complexes using X-ray diffraction methods[8] led to a different conclusion. In other words, the X-ray experiments performed at room temperature show that the nickel environment is square planar.[9] Caruso *et al.*[10] have made a comparative study of the mesogenic properties of some palladium(II), copper(II) and nickel(II) complexes. A higher thermal stability of the mesophase was found for the Pd(II) and Ni(II) complexes as compared to those of the corresponding copper(II) complexes. They have suggested that this might be due to higher stability of Pd(II) and Ni(II) towards a pseudotetrahedral distortion of the square planar coordinative geometry.

In order to examine the influence of the nature of the metal atom on the mesophase with the same ligand, the transition temperatures of two homologues

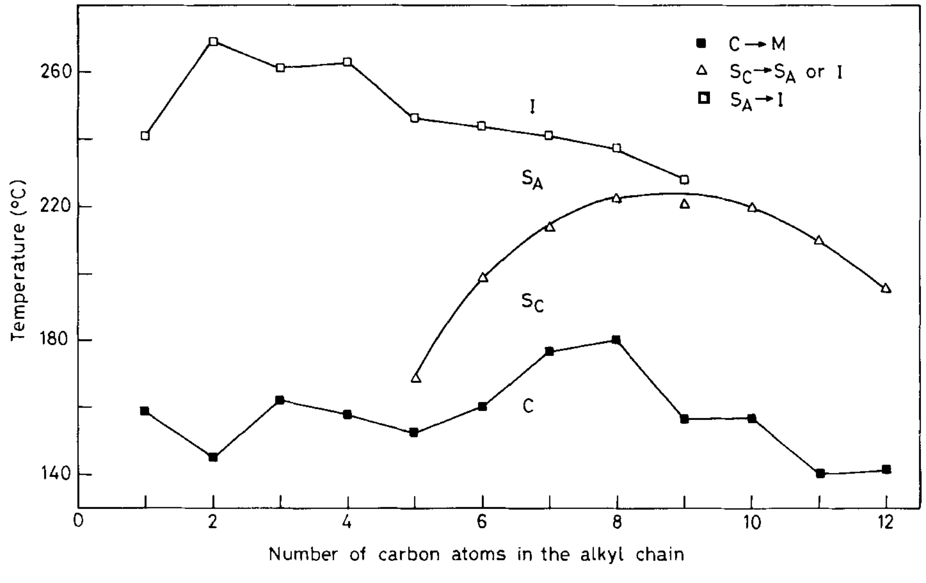
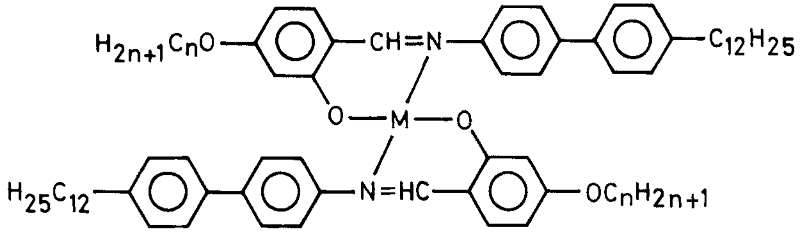


FIGURE 2 Plot of transition temperatures versus the number of carbon atoms in the alkyl chain for the nickel(II) complexes (A).

TABLE III

Transition temperatures (°C) of



n	M	C		S_C		S_A		I	Mesophase range(°C)
8	Cu[6]	.	206.0	.	224.0	.	255.5	.	49.5
8	Ni	.	180.0	.	222.0	.	237.0	.	57.0
8	Pd[6]	.	206.5	.	259.0	.	282.0	.	75.5
10	Cu[6]	.	201.0	.	229.0	.	243.5	.	42.5
10	Ni	.	157.0	.	220.0	.		.	63.0
10	Pd[6]	.	197.0	.	257.0	.	268.0	.	71.0

of each of Cu(II), Pd(II) and Ni(II) are given in Table III. It is seen that the order for thermal stability of the mesophase is Pd > Cu > Ni. This is in complete contrast to the *N*-alkylsalicylaldimine complexes of nickel(II) which have a higher thermal stability of the mesophase than the corresponding copper(II) complexes.[5] However, in all these cases the nickel complexes have the lowest melting points.

Salicylaldimine complexes of nickel(II) exhibit an anomalous magnetic behaviour. As far back as 1947 Willis and Mellor[11] found that the diamagnetic complex of bis(*N*-methylsalicylaldiminato)nickel(II) becomes paramagnetic when it is dissolved in 'inert' solvents such as benzene or chloroform. Preliminary experiments on magnetic measurements of polycrystalline samples of these nickel(II) complexes, (A) at room temperature using a Lewis coil force magnetometer indicate that they are diamagnetic. However, the broad bands obtained while recording the proton magnetic resonance spectra in chloroform clearly show that they are indeed paramagnetic. Further experiments are in progress to elucidate the magnetic behaviour of these complexes.

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