Nematic Liquid Crystal Materials containing Nickel(II) or Copper(II) Atoms. Two Different Kinds of Magnetic Behaviour

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It was found that the bis(*N*-R,4-decyloxybenzoyloxysalicylaldiminato) nickel(II) or copper(II) complexes (where R = n-C_nH_{2n+1}, n = 1—10) (series I and II respectively) formed enantiotropic nematic mesophases over a broad temperature range, with low melting points; e.s.r. and *X*-ray studies showed that these series exhibit different magnetic behaviour.

While thousands of organic compounds show a nematic mesophase,[1,2] only a few materials containing transition metals have been reported to show a nematic phase.[3,4,5] This mesophase, shown by some β-diketonato complexes of copper(II), was reported as a paramagnetic phase by Chandrasekhar *et al.*[4] Paramagnetism was also reported in the molten state of bis(*N*-alkylsalicylaldimine)nickel(II) complexes, which are diamagnetic in the solid state.[6] However, nickel complexes derived from this type of imines have not been described as liquid crystals to date.

Here, we report the liquid crystalline properties of two new series of *N*-alkylsalicylaldimine complexes of nickel(II) and of copper(II), namely series I and series II respectively.

The synthesis of the complexes was carried out using the method illustrated in Scheme 1. The complexes as well as the intermediates have all been characterized by C, H, N, microanalysis and i.r. and u.v.-vis. spectroscopies, for which satisfactory results were obtained.†

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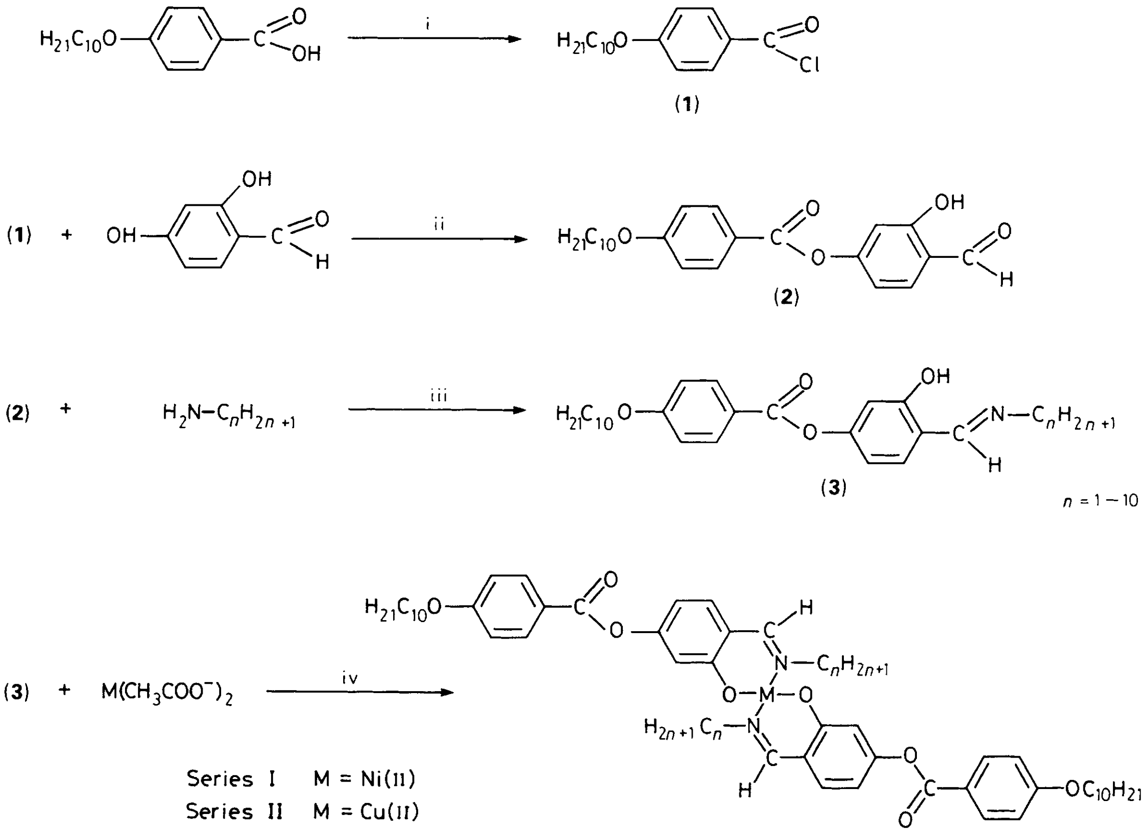
† Satisfactory elemental analyses were obtained for the complexes of series I and II.



Scheme 1. *Reagents and conditions*: i, $SOCl_2$, dimethylformamide (DMF), reflux, 2 h; ii, CH_2Cl_2, Et_3N, room temp., several hours; iii, EtOH, AcOH, reflux; iv, EtOH, reflux, 0.5 h.

Table 1. Transition temperatures (°C) and heats of transition (in italics) (kJ/mol) for nickel(II) complexes.

n	C_1		C_2		S_C		N		I	Range of L.C.[a]
1	.	125.6	.	241.5	(.	206.3)[b]	(.	213.9)[b]	.	
		39.9		*27.98*		*13.90*				
2	.	85.6	.	183.1	--------		(.	175)[b,c]	.	
		16.68		*56.6*						
3	.	130.8	.	168.4	--------		.	204.4	.	36.0
		18.48		*65.36*				*2.11*		
4	.	108.1	.	134.5	--------		.	168.3	.	33.8
		27.08		*90.06*				*2.09*		
5	.	126.8	--------	--------	--------		.	171.6	.	44.8
		79.51						*2.24*		
6	.	129.9	--------	--------	--------		.	168.0	.	38.1
		84.95						*1.23*		
7	.	92.5	.	126.6	--------		.	163.0	.	36.4
		8.27		*72.54*				*2.10*		
8	.	130.6	--------	--------	--------		.	158.3	.	27.7
		66.66						*2.02*		
9	.	130.1	--------	--------	--------		.	156.6	.	26.5
		68.40						*2.17*		
10	.	115.3	.	131.9	--------		.	154.6	.	22.7
		32.52		*37.57*				*1.28*		

[a] L.C. = liquid crystal. [b] The temperature in parentheses indicates a monotropic transition. [c] Optical data.

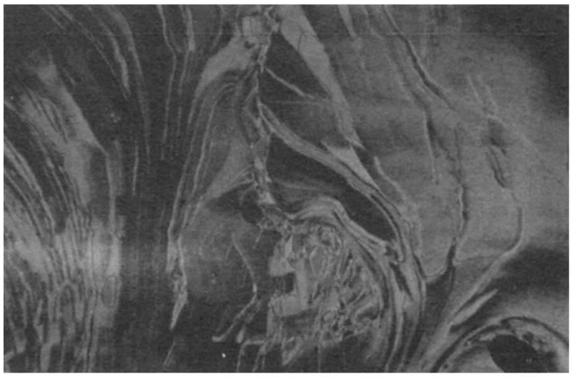


Figure 1. Photomicrograph of bis(*N*-hexyloxy, 4-decyloxybenzoyloxysalicylaldiminato)nickel(II) in its nematic phase at 155 °C viewed between crossed polars.

As far as we know, the compounds in series I are the first examples of liquid crystal nickel complexes derived from mono-imines and the compounds in series II are the first liquid crystal copper complexes derived from *N*-alkylsalicylaldimines reported to date.

Similar liquid crystal copper complexes have been previously reported[3,7,8] but they are all derived from *N*-4-phenylalkoxysalicylaldimines and they only show smectic phases, with the exception of the complexes reported by Ovchinnikov

Table 2. Transition temperatures (°C) and heats of transition (in italics) (kJ/mol) for copper(II) complexes.

n	C_1	C_2	S_C	N	I	Range of L.C.ᵃ
1	. 173.9	------	. 178.2	. 224.0	.	50.1
		64.92		*2.45*		
2	. 164.2	----------	----------	. 170.7	.	6.5
	64.55			*1.68*		
3	. 95.1	. 130.5	----	. 167.9	.	37.4
	21.95	*55.37*		*1.96*		
4	. 110.9	----------	----------	. 143.2	.	32.3
	73.57			*2.59*		
5	. 104.9	----------	----------	. 146.9	.	42.0
	88.18			*2.23*		
6	. 100.6	----------	----------	. 143.3	.	42.7
	83.81			*1.75*		
7	. 107.8	. 111.8	----	. 140.0	.	28.2
	46.20	*1.41*		*1.54*		
8	. 67.7	. 98.2	----	. 131.3	.	33.1
	6.18	*59.34*		*1.85*		
9	. 102.9	. 110.5	----	. 131.3	.	20.8
	56.06	*46.85*		*1.94*		
10	. 116.3	----------	----------	. 134.0	.	17.7
	56.29			*2.90*		

[a] L.C. = liquid crystal.

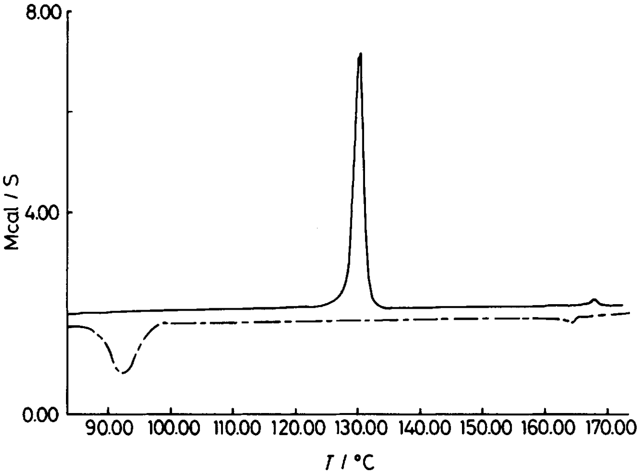


Figure 2. Differential scanning calorimetry profile for nickel(II) complex. Scan rate of 10 °C/min.

et al.[3] which, apart from the smectic phase, also show a nematic one. Also recently, disalicylidene–ethylenedimine complexes of nickel(II) and copper(II) have been described[9] which exhibit smectic A phases at high temperatures.

From studies with a Meiji optical microscope (equipped with polarizing light, a Mettler FP82 hot stage, and a FP80 central processor) and with a Perkin Elmer DSC-2 differential scanning calorimeter operated at a scanning rate of 10 °C/min on heating or cooling; [the apparatus was calibrated with indium (156.6 °C, 28.4 J/g) and tin (232.1 °C, 60.5 J/g) as standards], it was found that all the complexes synthesized were nematic liquid crystals (Tables 1 and 2). The textures were similar to that of a nematic phase shown by classical rod-like molecules.[10] A photomicrograph of the nematic phase can be observed in Figure 1.

For $n = 1$ both nickel(II) and copper(II) complexes, as well as the nematic phase, also show a smectic C phase at lower temperatures [monotropic in the case of Ni(II) and enantiotropic for Cu(II)].

The transition temperatures and enthalpies of the complexes of series I and II determined by DSC are gathered in Tables 1 and 2 respectively. The DSC profile of the series I complex is shown in Figure 2.

The stability of the complexes was tested by thermogravimetric analysis with a Perkin-Elmer TGS-2 equipped with a system 4 Microprocessor at a heating rate of 10 °C/min, under nitrogen. None of them show weight loss until 300 °C in the case of the nickel complexes, and 285 °C in the case of the copper complexes.

Nickel complexes have higher thermal stability of the mesophase than the copper complexes, but the latter have lower melting points.

E.s.r. studies carried out in three phases (polycrystalline, nematic, and isotropic) for complexes where $n = 10$ have shown that in the copper(II) complex the nematic phase is paramagnetic, whereas paramagnetism could not be observed with the nickel(II) complex.

Preliminary *X*-ray experiments have shown that both kinds of complexes behave differently when they are orientated by a magnetic field (nickel complexes have $\Delta\varkappa > 0$ and copper complexes have $\Delta\varkappa < 0$). Further experiments are in progress.

In conclusion, the results reported in this communication show that stable low temperature nematic liquid crystals can be obtained when *N*-alkyl-4-X-salicylaldimines are complexed with nickel(II) and copper(II). The nematic phase is paramagnetic in copper complexes and diamagnetic in nickel ones.

These complexes are good systems on which to carry out physical studies to elucidate their particular properties.

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