The liquid-crystalline properties of bis[*N*-[[4-[4-(alkoxy)benzoyloxy]2-hydroxyphenyl]methylene]alkanamino] complexes of Cu(II), Pd(II) and Ni(II). A general view

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The liquid-crystalline properties of bis[N-[[4-[4-(alkoxy)benzoyloxy]2-hydroxyphenyl]methylene]alkanamino] complexes of Cu(II), Pd(II) and Ni(II)

A general view

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The thermotropic liquid-crystalline phase behaviour of a homologous set of bis[N-[[4-[4-(alkoxy)benzoyloxy]2-hydroxyphenyl]methylene]alkanamino] copper(II) complexes is examined. New data are reported and taken into account in addition to those previously reported in this Journal. The influence of alkoxy and alkanamine groups on the nature and stability of the mesophase is underlined. As a general trend, with some notable exception, smectic (C type) mesomorphism is favoured by longer alkoxy and alkanamine chains. Data concerning some Pd(II) and Ni(II) homologous complexes are also reported. The mesophase stability (nematic phase) is higher for palladium and nickel complexes than for the copper containing homologues.

1. Introduction

A comparatively new family of liquid-crystalline compounds is obtained by utilizing organometallic complexation. Within this class of metallomesogens a significant number is based on tetracoordinated derivatives of Shiff's bases [1–11]. The synthesis and the liquid-crystalline behaviour of a number of homologous bis[N-[[4-[4-(alkoxy)benzoyloxy]2-hydroxyphenyl]methylene]alkanamino] metal complexes have been reported recently [8, 9]. Two homologous series of copper(II) complexes (herinafter referred to as n-mNCu) have been described in detail elsewhere [10, 11].
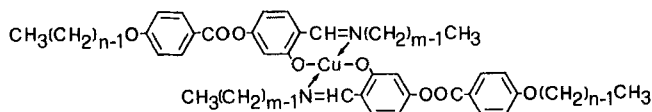
Nematic and/or smectic (C type) mesomorphism was observed depending on the number of carbon atoms in the alkoxy (n) and/or alkanamino (m) groups. Although as a general trend smectic mesomorphism is favoured by high n or m values (e.g. 6–1NCu is nematogenic while 14–1NCu is smectogenic), the influence of these parameters is interdependent and non-linear. For example, 14–2NCu is not mesomorphic, 14–6NCu is only nematogenic while 14–14NCu is both nematogenic and smectogenic [11].

We report here some quantitative results of a further investigation concerning a considerable additional number of homologous complexes whose liquid-crystalline
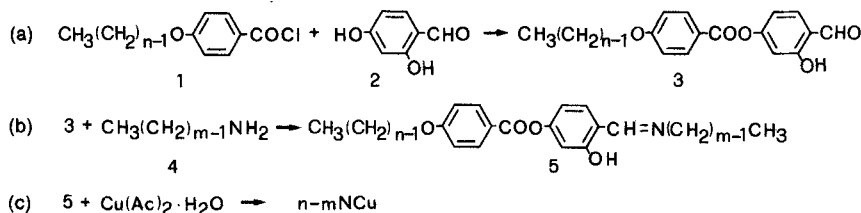
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phase behaviour was reported previously [8]. In order to study any specific influence of the nature of the metal atom on the liquid-crystalline properties, the investigation has been extended to some Pd(II) and Ni(II) containing homologues.

2. Experimental

The compounds which have been prepared and whose phase behaviour has been examined may be grouped as follows:

(1) n-mNCu ($n = 6, m = 1\text{--}15, 17; n = 10, m = 1\text{--}15, 17; n = 7\text{--}14, m = 8; n = 7\text{--}14,$
$m = 13$),

(2) n-mNPd ($n = 8\text{--}11, 14, m = 1; n = 7, m = 13; n = 8, m = 8, 13; n = 14, m = 3$),

(3) n-mNNi ($n = 8, 11, 14, m = 1; n = 12, m = 13$).

The chemical synthesis of the copper containing complexes is outlined in scheme 1. It was performed following a procedure described elsewhere [11]. The preparation of

(a) $CH_3(CH_2)_{n-1}O$—⟨ ⟩—$COCl$ + HO—⟨ ⟩—CHO → $CH_3(CH_2)_{n-1}O$—⟨ ⟩—COO—⟨ ⟩—CHO

          1   **2** OH   **3** OH

(b) **3** + $CH_3(CH_2)_{m-1}NH_2$ → $CH_3(CH_2)_{n-1}O$—⟨ ⟩—COO—⟨ ⟩—$CH=N(CH_2)_{m-1}CH_3$

        4   **5** OH

(c) **5** + $Cu(Ac)_2 \cdot H_2O$ → n-mNCu

Scheme 1.

palladium complexes was performed following a slightly different procedure at steps (*b*) and (*c*). This is outlined for 7–13NPd as an example.

0·288 g of aldehyde **3** ($n = 7$) and 0·141 g of amine **4** ($m = 13$) were dissolved in 20 ml of hot dioxane. The corresponding imine **5** ($n = 7, m = 13$) (in the following, the symbol n-mN will be used for imines containing n carbon atoms in the alkoxy segment and m carbon atoms in the alkanamine group), whose progressive formation was indicated by a deepening yellow colour of the solution, was not separated. A solution of 0·100 g of sodium acetate in 20 ml ethanol was added and, at a temperature close to 30°C, 0·136 g of $Pd(C_6H_5CN)_2Cl_2$ partially dissolved in 10 ml dioxane was finally added. The reaction mixture was brought to 60°C for 3 min. The yellow mixture was cooled to room temperature. The crystal phase was purified by chromatography (Florisil/chloroform) and successive recrystallization from chloroform/ethanol solution.

For the preparation of nickel containing complexes a similar procedure was followed. $Ni(ClO_4)_2 \cdot 6H_2O$ was used in the final step with ethanol in place of dioxane.

The chemical nature of some selected precursor aldehydes and imines as well as that of palladium and nickel containing complexes was monitored by ^{1}H-n.m.r. spectroscopy. Table 1 reports some selected n.m.r. data for a palladium complex as well as some imines **5**, namely 6–8N, 10–8N, 6–13N and 10–13N, whose phase behaviour was also examined. They are mesogenic; the transition temperatures are reported in table 1. As a further check, the copper content as CuO was quantiatively determined for a few copper containing complexes: 6–8NCu 8·21 per cent calculated, 8·26 per cent found; 10–8NCu 7·36 per cent calculated, 7·41 per cent found; 6–13NCu 7·17 per cent calculated, 7·18 per cent found; 10–13NCu 6·51 per cent calculated, 6·53 per cent found.

The phase behaviour of all compounds was examined by DSC thermal analysis (DSC-2 Perkin–Elmer apparatus) and by optical microscopy (Leitz polarizing microscope equipped with a Mettler FP 5 temperature controlled microfurnace). The ^{1}H-n.m.r. spectra were recorded on a 270 MHz Bruker spectrometer.

Table 1. Transition temperature for imines 6–8N, 10–8N, 6–13N, 10–13N and selected ^{1}H-n.m.r. data (δ/ppm, CDCl$_3$ solvent) for the same compounds (δ(im)) and for 8–13NPd (δ(Pd)).

	T_m/K	T_1/K	T_i/K	δ(im)	δ(Pd)	
6–8N	337·7		348·8	0·89 t	0·92 t	(–O(R)–CH$_3$)†
10–8N	341·6		351·9	4·04 t	4·05 t	(–CH$_2$–O–ϕ–)
6–13N				3·58 t	3·68 t	(=N–CH$_2$–)
10–13N	343·1	354·0	355·5	8·31	7·59	(–ϕ–CH=N)
				14·10		(–ϕ–OH)

Abbreviations: T_m, T_1, T_i = melting, liq. cryst.–liq. cryst. transition, isotropization temperatures respectively; t = triplet; no attribute = singlet; –ϕ– = p-phenylene group. † Average values.

Homologous values of δ measured for different imines may differ by +1 in the last digit; temperatures are measured at the maximum of the DSC transition endotherm at the first heating run of samples crystallized from solution.

3. Results and discussion

All but one of the copper complexes and most of those containing palladium show enantiotropic mesomorphic behaviour; 6–2NCu is only monotropically mesomorphic; enantiotropic mesomorphism is exhibited by the four nickel complexes examined. The optical textures indicate that the large majority of compounds are nematogenic (shown by a very mobile schlieren texture), some also show smectic C mesomorphism while for three of them only smectic C mesomorphism (shown by schlieren or schlieren and fan textures) is observed.

As it was already noticed for series n-1NCu and 14-mNCu, most compounds exhibit solid state polymorphism. This may occur either because different solid phases are stable as a function of temperature or because the melt crystallized solid is different from the solution cyrstallized one. Frequently, both cases occur together. A detailed description of the solid phase behaviour, even if only thermal and optical microscopy data are used, goes beyond the scope of this paper. Some account is given in tables 2 and 3 which, however, report melting temperatures of solution crystallized samples only. A more detailed description is made for only a few cases to help understand the liquid-crystalline behaviour.

3.1. *Copper complexes*

Thermodynamic data concerning copper complexes are reported in tables 2 and 3. As a general trend, as n and m increase both melting and isotropization temperatures decrease with a decreasing gradient. The thermal stability interval of the mesophase ($T_{NI} - T_{CN}$) shows sharp variations with m only for small values of m. It has its minimum value for $m=2$. In fact, no mesomorphism was observed for 14–2NCu [11], monotropic mesomorphism is exhibited by 6–2NCu and a stability interval of 6·4 K is measured for the nematic phase of 10–2NCu as compared to 45·6 K and 38·5 K found for 10–1NCu and 10–3NCu, respectively.

No relevant odd–even fluctuation of the nematic–isotropic transition temperature and of the corresponding enthalpy changes (ΔH_{NI}) occurs with any regularity within the members of a homologous series. A comparative examination of the data shows that the effects of the alkanamino and alkoxy terminals on the thermal parameters are quantitatively comparable. However, some systematic differences occur concerning

both the influence on the nature of the mesophase exhibited and on the phase transition parameters. For ease of comparison, table 4 reports melting and isotropization temperatures for some pairs of complexes, $n_1 - m_1 NCu$ and $n_2 - m_2 NCu$, having $n_1 + m_1 = n_2 + m_2$ and $n_1 = m_2$ (or $n_1 \approx m_2$) and $m_1 = n_2$ (or $m_1 \approx n_2$). With a single exception, it is apparent that, within each pair, the compound having higher m has also higher T_{CN} and T_{NI}. So, the alkanamino terminals appear to be somewhat more efficient stabilizers of the mesophase than the alkoxy ones.

Concerning the influence of the terminal chains on the mesophase nature, table 5 summarizes the results for the entire set of compounds. As a general trend, smectic mesomorphism is favoured by longer alkanamino or alkoxy terminals. The influence of both terminal types appears to be cooperative. However, a peculiar exception is the sharp destabilization of the smectic phase observed for compounds 10-$nNCu$ and 14-$nNCu$ for $n > 1$. To explain this feature, which is presumably connected also with the aforementioned drop of the thermal stability interval of the mesophase at least qualitatively, we have no suggestion.

As to the influence on the nature of mesophasic behaviour, alkoxy and alkanamino terminals do not play an entirely symmetrical role. For example, the first member of series 14-$mNCu$ showing smectic mesomorphism, although in monotropic form, has $m = 10$ while analogous behaviour is exhibited for n as low as 6 for compounds n-14NCu. In a similar way, while compound 8–13NCu is enantiotropically smectogenic, 13–8NCu is not.

Table 2.   Transition temperatures of copper complexes n-$mNCu$ at the onset of the DSC endothermic signal.

n	m	T_m/K	$\Delta H_m/\text{kJ mol}^{-1}$	T_{SN}/K	$\Delta H_{SN}/\text{kJ mol}^{-1}$	T_{NI}/K	$\Delta H_{NI}/\text{kJ mol}^{-1}$
6	8	388·7	(b)			427·1	2·44
7	8 (a)	382·6	(b)			420·7	2·46
8	8	381·4	(b)			418·3	2·56
9	8	382·8	57·4			412·7	2·51
10	8	376·2	63·8			409·8	2·64
11	8	377·7	(b)			405·2	2·58
12	8	372·5	(b)			402·2	2·76
13	8	375·1	(b)			398·4	2·74
14	8	372·8	142·2			395·9	2·88
6	13 (a)	403·3				409·1	3·33
7	13	373·2	81·2	(c)		407·0	3·54
8	13 (d)	382·6	25·6	392·3	10·1	406·8	3·93
9	13 (e)	377	35·3	393·2	11·4	404·5	4·38
10	13	385·2	81·4	393·6	12·1	405·9	4·84
11	13	388·7	84·1	393·2	11·9	401·3	4·95
12	13	389·0	91·3	392·0	11·3	400·1	5·12
13	13	384·6	93·3	392·4	12·4	398·1	5·18
14	13	384·4	100·4	391·6	12·6	396·6	5·12

$\sigma T/T = 0·001$ for four figures values, $0·005$ for the others. n, $m =$ Number of carbon atoms in the alkoxy (n) and alkanamine (m) groups; $T_m =$ melting temperature of the solution crystallized solid; $T_{SN} =$ smectic–nematic transition temperature; $T_{NI} =$ nematic–isotropic transition temperature; $\Delta H =$ molar enthalpy change at the phase transitions; $0·05 > \sigma \Delta H / \Delta H > 0·01$.

(a) Solid phase transition observed; (b) not measurable because of recrystallization phenomena; (c) two monotropic smectic phases observed (see text); (d) solid phase transition at 377·6 K, $\Delta H = 95·4 \text{ kJ mol}^{-1}$; (e) solid phase transition at 363·7 K, $\Delta H = 78·9 \text{ kJ mol}^{-1}$.

Table 3.   Thermodynamic data for the phase transitions (see table 2 for explanations).

n	m	T_m/K	$\Delta H_m/kJ\,mol^{-1}$	T_{SN}/K	$\Delta H_{SN}/kJ\,mol^{-1}$	T_{NI}/K	$\Delta H_{NI}/kJ\,mol^{-1}$
6	1	484·7	58·0			539·1	2·87
6	2	488·9	60·6			485	
6	3	441·8	47·7			479·4	2·89
6	4	422·7	58·2			448·6	2·60
6	5	403·4	42·8			448·0	2·56
6	6	403·6	(b)			441·0	2·55
6	7	399·0	(b)			439·3	2·63
6	8 (a)	388·7	(b)			427·1	2·44
6	9 (a)	394·7	39·7			424·2	2·66
6	10 (a)	393·5	(b)			418·2	2·71
6	11 (a)	401·1	53·4			416·2	3·13
6	12	398·8	53·1			411·2	2·99
6	13 (a)	403·3	(b)			409·1	3·33
6	14	394·4	43·4 (c)			405·4	3·71
6	15 (a)	387·3	38·2	394·4		403·6	4·19
6	17 (a)	381·4	57·9 (d)	395·9		399·7	18·6 (c)
10	1 (e)	452·8	31·5	456·9	0·63	498·4	2·54
10	2	438·9	65·6			445·3	2·58
10	3	406·3	51·3			444·5	2·65
10	4	390·1	84·9			417·0	2·43
10	5	381·4	76·4			419·8	2·37
10	6 (a)	390·0	(b)			417·9	2·52
10	7	385·2	44·2			418·7	2·59
10	8	376·2	63·8			409·8	2·64
10	9 (a)	388·3	(b)			410·0	2·72
10	10	388·9	55·6			407·2	3·02
10	11 (a)	393·4	(e)	(f)		407·1	3·39
10	12	379·4	116·1	387·2	7·72	404·4	3·59
10	13	385·2	81·5	393·6	12·10	405·9	4·84
10	14	387·5	64·8	396·7		401·7	18·7 (c)
10	15	391·5	71·0	399·5		400·9	20·3 (c)
10	17	396·4	78·9 (g)			400·6	23·2 (h)

(a) Solid phase transition observed; (b) not measurable because of recrystallization phenomena; (c) includes the contribution of an unresolved SN phase transition; (d) includes the contribution of a solid phase transition; (e) not measurable because a second solid phase melting at a higher temperature is present in a variable amount; (f) smectic mesomorphism is monotropic, $T_{SN} = 381$ K (optical observation); (g) measured as $\Delta H_{CI} - \Delta H_{SI}$, C = crystal phase; (h) SI phase transition.

Table 4.   Melting and isotropization temperatures for pairs of copper complexes $n1 - m1NCu$ and $n2 - m2NCu$ characterized by having $n1 + m1 = n2 + m2$ and $n1 = m2$ or $n1 \approx m2$.

$n1$	$m1$	T_m/K	T_i/K	$n2$	$m2$	T_m/K	T_i/K
6	10	393·5	418·2	10	6	390·0	417·9
10	10	388·9	407·2	12	8	372·5	402·2
10	12	379·4	404·4	14	8	373·0	395·9
6	13	403·3	409·1	14	5	386·3	401·7
7	13	373·2	407·0	14	6	384·0	401·0
8	13	382·6	406·8	13	8	375·1	398·4
6	14	394·4	405·4	14	6	384·0	401·0
10	14	387·5	401·7	14	10	380·4	397·0

Data for complexes 14-mNCu are taken from [11].

Table 5.   Mesophasic behaviour of complexes n-mNCu. N(m) and S(m) indicate nematic or smectic monotropic mesomorphism.

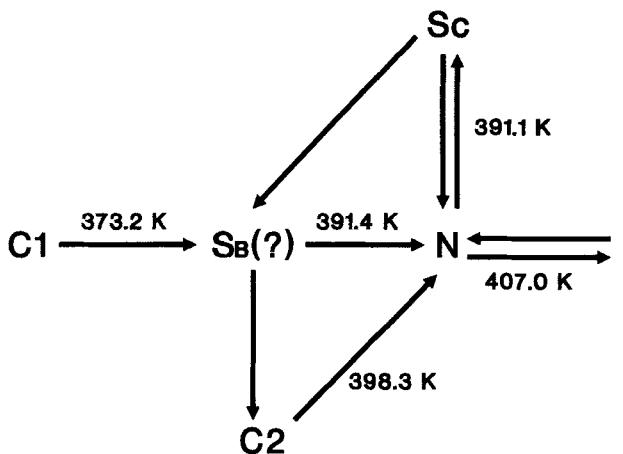| m	6	7	8	9	10	11	12	13	14
					n				
1	N	N	N	N	N,S	N,S	N,S	N,S	S
2	N(m)				N				
3	N				N				N
4	N				N				N(m)
5	N				N				N
6	N				N				N
7	N				N				N
8	N	N	N	N	N	N	N	N	N
9	N				N				N
10	N				N				N,S(m)
11	N				N,S(m)				N,S(m)
12	N				N,S				N,S
13	N	N,S(m)	N,S	N,S	N,S	N.S	N,S	N,S	N,S
14	N,S(m)				N,S				N,S
15	N,S				N,S				S
17	N,S				S				

7–13NCu also shows a highly ordered monotropic smectic phase.

The liquid crystalline properties of complexes 10-mNCu with m = 1–10 have already been reported by Serrano *et al.* [9]. As far as mesophasic behaviour is concerned, our findings are in complete accord. However, some quantitative differences have been found concerning isotropization temperatures and enthalpies. In fact, while for complexes with m = 1, 4, 5, 10 the agreement is excellent, systematically lower values are reported by Serrano *et al.* for the other compounds (e.g. $T_{NI} = 413 \cdot 1$ K, $\Delta H_{NI} = 1 \cdot 54$ kJ mol^{-1} for 10–7NCu, as compared to the values of $418 \cdot 7$ K and $2 \cdot 59$ kJ mol^{-1} reported in table 3). These differences appear not to be connected with some inconsistency that is also found if the melting temperatures are compared. Probably, such inconsistency should be traced to the tendency to exhibit solid phase polymorphism which characterizes many of these compounds.

We shall now discuss in greater detail the phase behaviour of a few compounds taken as an example.
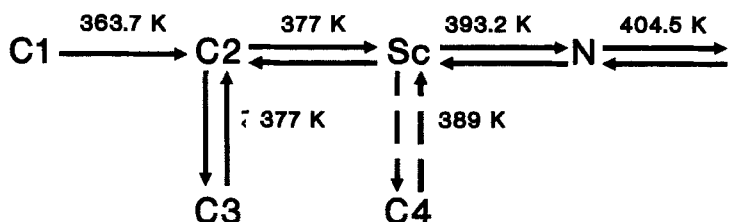
3.1.1. *Compound 7–13NCu*

The phase behaviour of 7–13NCu is sketched in scheme 2. Phase C_1, which forms by solution crystallization, melts at $373 \cdot 2$ K producing a very viscous phase with mosaic textures similar to those reported in the literature for ordered smectic phases such as S_B [12]. On heating, this ordered smectic transforms at $391 \cdot 4$ K into a nematic phase characterized by a very mobile schlieren texture. However, even at constant temperature, the ordered smectic undergoes crystallization producing a solid phase C_2 which is stable at room temperature and melts at $398 \cdot 3$ K to the nematic phase. On cooling this phase at a rate not higher than 10 K/min, a new liquid-crystalline phase forms whose most common texture (shown by a fan and schlieren texture) identifies it as a S_C. The reverse transformation takes place at $391 \cdot 1$ K. On cooling the smectic C phase, the ordered smectic characterized by a mosaic texture forms closing thus a cyclic

$$
\begin{array}{c}
\mathbf{Sc} \\
\nearrow \quad \uparrow\downarrow \ \ 391.1\ K \\
C1 \xrightarrow{373.2\ K} S_B(?) \xrightarrow{391.4\ K} N \rightleftharpoons I \\
\downarrow \quad \nearrow \quad 407.0\ K \\
398.3\ K \\
\mathbf{C2}
\end{array}
$$

Scheme 2.

transformation which can be reproduced at will. In conclusion, the liquid-crystalline behaviour of 7–13*N*Cu exhibits two monotropic smectic phases if a melt crystallized sample is examined, while with the solution crystallized solid, only the S_C phase is monotropic. It is worth noting that a sample which is solution recrystallized after having undergone a thermal cycle (including isotropization) reproduces the behaviour of a previously untreated sample.

3.1.2. *Compound 9–13NCu*

$$
\begin{array}{c}
C1 \xrightarrow{363.7\ K} C2 \underset{}{\overset{377\ K}{\rightleftharpoons}} Sc \underset{}{\overset{393.2\ K}{\rightleftharpoons}} N \underset{}{\overset{404.5\ K}{\rightleftharpoons}} I \\
\uparrow\downarrow\ 377\ K \qquad \uparrow\downarrow\ 389\ K \\
C3 \qquad\qquad C4
\end{array}
$$

Scheme 3.

The phase behaviour of 9–13*N*Cu is summarized by scheme 3. The sequence of phase transitions observed on heating a solution crystallized sample is $C_1 \to C_2 \to S_C \to N \to I$. Both liquid-crystalline phases are enantiotropic and the schlieren texture is that most frequently observed. A solid phase transition occurs also on cooling. However, on successive heating, the phase stable at room temperature (C_3) transforms into C_2 at a temperature so close to $T_{C_2 S_C}$ that melting and solid-phase transition endotherms coalesce. The behaviour of melt crystallized samples is reproducible in successive thermal cycles. However, by annealing the smectic C phase at about 380 K, a different solid phase, C_4, forms. The amount of C_4 formed depends on the annealing time. C_4 does not undergo any solid phase transition and melts at 389 K producing the smectic C phase. No effect on the liquid-crystalline behaviour is produced other than a reduction of the thermal stability interval of the smectic phase due to the higher melting temperature of C_4.

Table 6. Influence of the metal atom on the transition temperatures (*a*) (see table 2 for explanations).

		Me = Cu(II)		Me = Pd(II)		Me = Ni(II)	
n	*m*	T_m/K	T_{NI}/K	T_m/K	T_{NI}/K	T_m/K	T_{NI}/K
8	1	484·7	539·1	513·4	536·7	537·7	543·5
9	1	459·4	505·9	510·0	524·1		
10	1	452·8	498·4	510·5	514·5		
11	1	449·0	491·1	507·6	—	523 (*b*)	532
14	1	440·8	477·3 (*c*)	501·2	—	505 (*b*)	523
14	3	408·4	422·8	446·6	470·4		
8	8	381·4	418·3	428·1	468·3		
7	13	373·2	407·0	440·1	444·3		
8	13	382·6	406·8	437·4	442·3		
12	13	389·0	398·1			403·0	415·7

(*a*) All Pd(II) and Ni(II) complexes exhibit a solid phase transition; (*b*) both T_m and T_{NI} from optical observations; (*c*) SI phase transition.

3.2. *Palladium and nickel complexes*

The thermal data concerning the phase behaviour of Pd and Ni containing complexes are reported in table 6. Most complexes exhibit nematic mesomorphism and their melting and isotropization temperatures exceed those of the corresponding copper containing homologues. Analogous differences were observed by Serrano *et al.* [9] for homologous copper(II) and nickel(II) complexes and for other mesogenic salicylideneaminates of copper(II) and palladium(II) [6]. An explanation for this behaviour, which is under scrutiny, might be the higher stability of Pd(II) and Ni(II) complexes towards a pseudo-tetrahedral distortion of the square planar coordinative geometry. Actually, single crystal X-ray diffraction analysis of the crystal structure of bis{4-(*n*-heptyloxy)-*N*-[*p*-(*n*-hexyloxy)phenyl]salicylidene-aminato}palladium(II) [13] has shown that the coordinative geometry is strictly square planar while this geometry and a distorted tetrahedral one are both present in equal amounts in the crystal phase of the copper(II) homologue [14]. (Melting and isotropization temperatures of these compounds are: $T_{CN} = 444$ K, $T_{NI} = 488$ K for the Pd(II) complex; $T_{CN} = 423$ K, $T_{NI} = 441$ K for the Cu(II) containing homologue) [6].

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