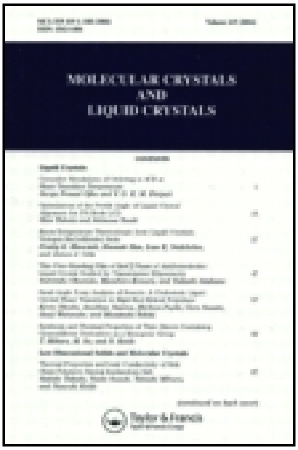

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Transition Metals Complexed to Ordered Mesophases[1]. Synthesis and Mesomorphic Properties of a Homologous Series of N-(4-Dodecyloxysalicylidene)-4′-Alkylanilines Complexed to Palladium(II)

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Transition Metals Complexed to Ordered Mesophases[1]. Synthesis and Mesomorphic Properties of a Homologous Series of *N*-(4-Dodecyloxysalicylidene)-4′-Alkylanilines Complexed to Palladium(II)

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The new [*N*-(4-dodecyloxysalicylidene)4′-C_nH_{2n+1}-aniline] palladium (II) derivatives, $(R_nL)_2Pd$, (**1**–**6**: $n = 1$–4, 6, 8 respectively) have been synthetized and their mesomorphic properties investigated by optical microscopy, DSC and X-ray diffraction measurements. Complexes **1**–**6**, but **4**, display a monotropic (**1**, **5**) or enantiotropic (**2**, **3**, **6**) smectic *A* mesophase. In **1**–**6** the geometry of the metal coordination sphere is square planar and with reference to homologous $(R_nL)_2M$ compounds the mesomorphism of **1**–**6** appears at temperatures higher than for $(R_nL)_2VO$ (distorted square pyramidal) or $(R_nL)_2Cu$ (distorted square planar).

INTRODUCTION

The metallo-mesogens form a sub-class of liquid crystalline compounds whose molecules are featured by incorporation of transition metal atoms into a mesogenic structure(2,3). Thermotropic ligands as salicylideneimines (L) are known to form L_2M complexes(4) with a number of M(II) ions, therefore with reference to metallo-mesogens, they are helpful starting materials for investigation dealing with the relationships among nature of the metallic centre, coordination geometry and mesomorphic properties.

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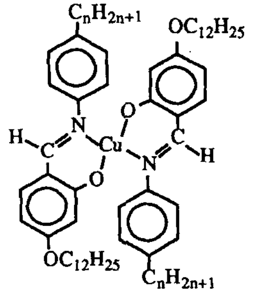
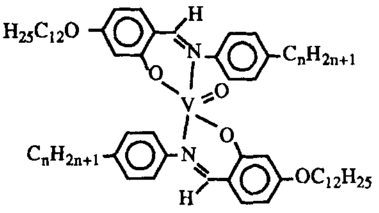
In a previous paper[(6b)] we compared copper, **I**, and vanadyl, **II**, mesogens (respectively distorted square planar[(4)] and distorted square pyramidal[(5)] complexes) **II**. Herein we consider the square planar geometry as it results from palladium (II) coordination[(4)].



$(R_nL)_2Cu$

n=1,2,3,4,6,8

I



$(R_nL)_2VO$

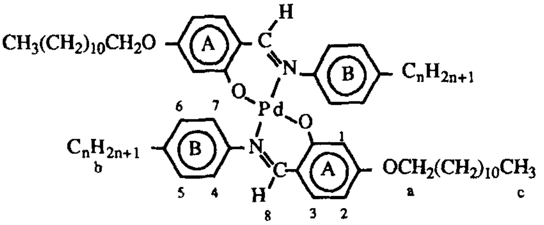
n=1,2,3,4,6,8.

II

Actually several L_2M mesogens, M = Cu(II)[(7)], VO(II)[(8)] and Pd(II)[(9,8b)] have been reported in the literature, however a proper evaluation of the differences induced by each of the various coordination sphere fail because of the different substituents bonded to L. Consequently, as complexes bearing the same L ligands, the homologous series of $(R_nL)_2Pd$ complexes, wherein R_nL are the *N*-(4-dodecyloxysalicylideneiminate)-4'-C_nH_{2n+1}-anilines of series **I** and **II**, has been synthetized and characterized.

EXPERIMENTAL

The synthesis of the palladium complexes $(R_nL)_2Pd$, **1–6**, having general formula **III** was achieved reacting the R_nLH ligand ($n = 1$–$4, 6, 8$ respectively),[(6a)] with sodium hydroxide and $Pd(PhCN)_2Cl_2$[(10)] in molar ratios as 2:2:1. [As an example to 100 mg of R_1LH dissolved in dioxane (5 mL) were added 1 mL of an ethanolic solution containing an equimolar amount of sodium hydroxide and $Pd(PhCN)_2Cl_2$ (48 mg) dissolved in dioxane (3 mL) Yield 64%].



1-6: n=1, 2, 3, 4, 6, 8 respectively

III

The compounds **1–6** were obtained, after recrystallization from chloroform-ethanol, as yellow microcrystalline solids whose elemental analyses agree with the expected

TABLE I

Microanalytical Data for Compounds **1**–**6**.

		Found (calculated)		
Compd.	Formula	C	H	N
1	$C_{52}H_{72}N_2O_4Pd$	69.70 (69.73)	8.10 (8.10)	3.11 (3.14)
2	$C_{54}H_{76}N_2O_4Pd$	70.46 (70.21)	8.26 (8.29)	2.86 (3.04)
3	$C_{56}H_{80}N_2O_4Pd$	71.05 (70.67)	8.57 (8.47)	2.97 (2.95)
4	$C_{58}H_{84}N_2O_4Pd$	71.36 (71.11)	8.92 (8.64)	2.91 (2.86)
5	$C_{62}H_{92}N_2O_4Pd$	71.99 (71.88)	9.03 (8.95)	2.44 (2.71)
6	$C_{66}H_{100}N_2O_4Pd$	72.85 (73.11)	9.35 (9.29)	2.42 (2.59)

stoichiometry. The yields are between 40 and 70%. The complexation to the metal atom is confirmed by ^{1}H NMR spectroscopy. Indeed with respect to the uncoordinated ligand, for each complex a highfield shift of the methinic proton (H_8: $\delta = 7.55$ and $\delta = 8.57$ in **III** and in R_nLH respectively) is observed and, in any case, the aromatic part of the ^{1}H NMR spectra shows two sets of signals attributable respectively to the *AA'BB'* spin system of the benzene rings *B* ($\delta = 7.20$) and to the protons of the palladium bonded phenyl rings, *A*, (H_1, $\delta = 5.56$; H_2, $\delta = 6.14$; H_3, $\delta = 7.01$). In addition, the protons H_1, with reference to the homologous protons in R_nLH, are found highfield shifted in $(R_nL)_2Pd$. Since such a shift can be due to the magnetic shielding exerted by the close phenyl group, *B*,$^{(11)}$ the ^{1}H NMR spectra could account also for a *trans* arrangement of N (and O) donor atoms$^{(12-18)}$ as shown in **III**.

Analytical data are given in Table I and representative ^{1}H NMR (Bruker AW300, $CDCl_3$, tetramethysilane internal standard) data, as an example, are reported for the complex $(CH_3L)_2Pd$:
δ7.55 (s, H_8); δ7.20 (m, H_4, H_5, H_6, H_7) ;δ7.01 (d, H_3, J (H_3, H_2) = 8.8 Hz); δ6.14 (dd, H_2, J(H_2, H_3) = 8.8 Hz; J(H_2, H_1) = 2.3 Hz); δ5.56 (d, H_1, J(H_1, H_2) = 2.3 Hz); δ3.79 (t, H_a); δ2.40 (s, H_b); δ0.9 (t, H_c).

RESULTS AND DISCUSSION

Complexes **1**–**6** are mesogens. The textures of the mesophases were observed with a Zeiss Axioscope polarising microscope equipped for photography and with a Linkam CO 600 heating stage while the thermal behaviour was monitored by means of a Perkin Elmer DSC 7 (calibrated with indium 156.6°C, 28.4 J/g) at a heating rate of 5°C min^{-1}. The transition temperatures and thermodynamic data are summarized in Table II.

All of the **1**–**6** compounds but **4** exhibit a smectic *A* phase which was identified from the appearance of the focal conic fan texture (**1**, **3**, **5** and **6**) or from the homeotropic texture (**2**)$^{(19)}$. The occurrence of the mesophases along the homologous series follows an anomalous trend which we are not able to explain. The S_A phase is monotropic for **1** ($n = 1$); it becomes enantiotropic for **2** and **3** ($n = 2, 3$), but for **4** ($n = 4$) it disappears and only a solid to isotropic transition is observed. The next homologous term of the series, **5**, ($n = 6$) displays once again a monotropic S_A phase which becomes enantiotropic for **6** ($n = 8$). The progressive lengthening of the alkyl chains causes a raising of

TABLE II

Transition Temperatures, Enthalpies and Mesophases for Compounds **1–6**.

Compd.	Transition	T°C	ΔH (J/g)
1	K_1–K_2	116.4	24.85
	K_2–I	179.0	37.14
	I–S_A	173.3	5.73
	S_A–K_2	152.5	27.55
	K_2–K_3	112.6	23.83
2	K_1–K_2	126.1	14.69
	K_2–S_A	157.8	24.71
	S_A–I	182.2	8.81
	I–S_A	176.2	8.02
	S_A–K^*	119.7	36.90
3	K_1–K_2	113.6	68.10
	K_2–S_A	177.9	11.27
	S_A–I	195.9	11.12
	I–S_A	195.2	9.59
	S_A–K_2	162.6	12.94
	K_2–K_3	102.2	70.60
4	K_1–K_2	90.5	11.59
	K_2–I	203.2	27.91
	I–K_2	198.2	27.11
	K_2–K'_2	87.8	12.28
5	K_1–K_2	57.6	8.48
	K_2–I	187.5	35.90
	I–S_A	181.2	7.23
	S_A–K_3	176.9	17.61
	K_3–K'_3	53.8	6.62
6	K_1–S_A	171.6	16.89
	S_A–I	175.5	4.51
	I–S_A	174.9	6.46
	S_A–K_2	162.2	18.92

K^* = solid phase with a low degree of crystallinity.

the clearing temperatures until **4** followed by a fall for **5** and **6**. There is no evidence of the even-odd alternation along the series.

The structural features of the different mesophases were determined by X-ray diffraction measurements performed with the INEL CPS-120 powder diffractometer, equipped with a position sensitive detector covering a scattering angle of 120°, with an angular resolution of 0.0018°. Monochromatized Cu–K_α radiation ($\lambda = 1.54$ Å) was used. The samples, 1 mm thick, were placed between two thin Al sheets, fixed to a circular hole (1 cm diameter) in an Al matrix. Heating was achieved by a hot stage containing electric resistors and the temperature of the sample was controlled by a temperature regulator to ± 0.1°C. The results of the X-ray experiments confirmed the above described mesomorphism. The values d_{SA} of the layer thickness in the smectic phases, measured from the X-ray diffraction spectra, are reported in Table III.

The smectic periodicity does not seem to vary in a regular fashion with the number n of methylene groups in the alkyl-chains: it is essentially constant for the first terms, **1–3**, of the series (about 30 Å) while a progressive increase is observed in **5** and **6** where it

TABLE III

Layer Thickness in the Smectic *A* Phases for the Homologous $(R_nL)_2M$ (M = Pd, Cu, VO) Compounds.

n	$(R_nL)_2Pd$	$(R_nL)_2Cu$	$(R_nL)_2VO$
1	$d_{S_A} = 29.7$ Å	$d_{S_A} = 25.0$ Å	
2	$d_{S_A} = 30.4$ Å	$d_{S_A} = 30.0$ Å	
3	$d_{S_A} = 30.3$ Å	$d_{S_A} = 30.2$ Å	
4		$d_{S_A} = 30.8$ Å	$d_{S_A} = 29.0$ Å
6	$d_{S_A} = 31.9$ Å		$d_{S_A} = 31.0$ Å
8	$d_{S_A} = 32.8$ Å		$d_{S_A} = 30.9$ Å

takes the values 31.9 Å and 32.8 Å, respectively. In addition, no significative variation of the periodicity with the temperature is observed. All the **1–6** species exhibit solid state polimorphism. As an example of the mesomorphic behaviour of the whole series, Figures 1 and 2 show the X-ray diffraction spectra obtained at different temperatures during a complete thermal cycle for compounds **3** and **5**, respectively.

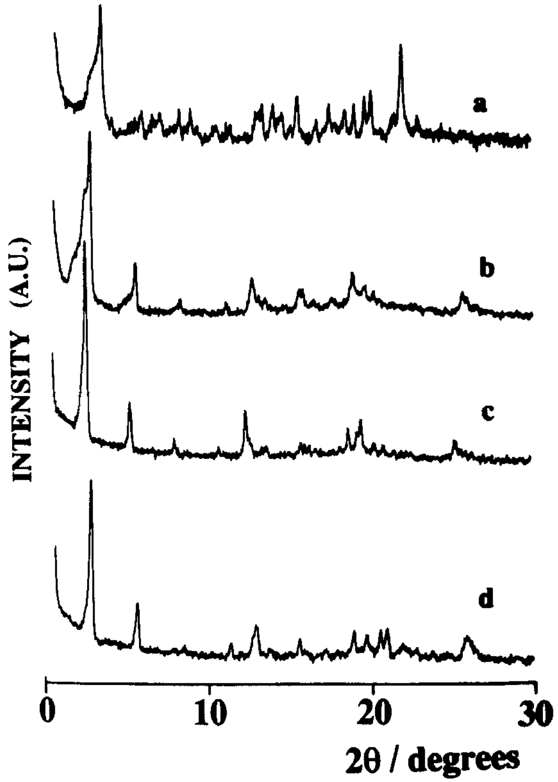


FIGURE 1 X-ray diffraction patterns of compound 3 obtained at different temperatures during a complete thermal cycle. Heating cycle: a) room temperature; b) $T = 150°C$; c) $T = 190°C$. Cooling cycle: d) $T = 190°C$; e) $T = 150°C$; f) $T =$ room temperature.

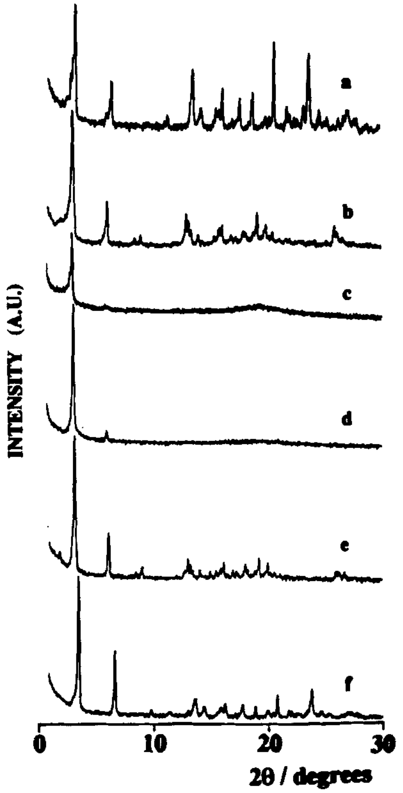


FIGURE 2 X-ray diffraction patterns of compound **5** obtained at different temperatures during a complete thermal cycle. Heating cycle: a) room temperature; b) $T = 100°C$. Cooling cycle: c) $T = 170°C$; d) room temperature.

All the solid phases, except the room temperature solid phase of **2**, after a thermal cycle exhibit a very high degree of cristallinity. Concerning the smectic phases, the X-ray diffraction patterns evidence for all compounds a considerable sharpness of the characteristic low angle diffraction peak (Figure 1c–d), which indicates a strong correlation between adjacent smectic layers. In addition, the smectic X-ray diffraction spectra of **1–3** shows the presence of the second order Bragg reflection on the smectic layers, which is not quite usual. This reflects an electron density distribution along the normal to the smectic layers which can not be described by a single sinusoidal modulation(20). Moreover, the consideration that the intensity ratios between first and second order is essentially the same for the three compounds suggests a similar electron density distribution, which comes from a similar molecular arrangement normally to the smectic layers.

The mesomorphic behaviour of compound **5** in the cooling cycle deserves a particular comment. The S_A mesophase as observed by optical microscopy (Figure 3) revealed a certain degree of instability due to an incipient crystallization connected to the incoming solid phase. This effect revealed to be strongly dependent on the cooling conditions and in particular on the cooling rate. This behaviour is probably related to the very narrow thermal stability range of the mesophase caused by the partial superposition of the transition temperature ranges associated to the isotropic-to-smectic and smectic-to-solid transitions, as shown by the DSC curve. A similar behaviour of the compound was observed in the X-ray diffraction measurements. This caused a difficulty in recording the spectrum of the S_A phase before the crystallization peaks could form. The spacing of the smectic layers has been calculated from the peak corresponding to the main periodicity in the diffraction pattern of the solid phase (see Figure 2C).

Palladium complexes bearing salicylideneaniline ligands have been previously reported(9a–c,8b). The complexed ligands belong to three different series: *N*-(4-alkoxysalicylidene)-4′-alkoxyanilines, (**IV**), *N*-(4-alkanoyloxysalicylidene)-4′-alkanoyl- oxyanilines, (**V**), *N*-(4-*n*-alkoxybenzoyloxyicylidene)-4′alkylamine, (**VI**) and *N*-(4-alkoxybenzoyloxysalicylidene)-4′-*n*-butylaniline (**VII**) respectively. Complexes obtained from **IV**(9a,8b) and **V**(9a) exhibit smectic C and A polymorphism. Contrarily, for the **VI** derivatives(9c) nematic phases only have been detected while for the **VII**'s one, namely *N*-(4-hexadecyloxybenzoyloxysalicylidene)-4′-*n*-butylaniline,(9b) both smectic and nematic mesophases are present.

The ligands **IV–VII** have been reacted also with copper (II). The comparison between Cu(II) and Pd(II) homologous complexes arising from ligands **IV–VI** highlights the increase of melting and clearing temperatures for the palladium-containing species(9a,c). A different situation has been found in palladium and copper derivatives of **VII**(9b). The palladium complex shows lower melting and clearing temperatures than the analogous copper complex.

In the present case a more extensive comparison with the homologous copper and vanadyl complexes is allowed (Figure 4). Firstly the incorporation of the palladium atom in the organic ligand induces a raising of the clearing temperatures. The

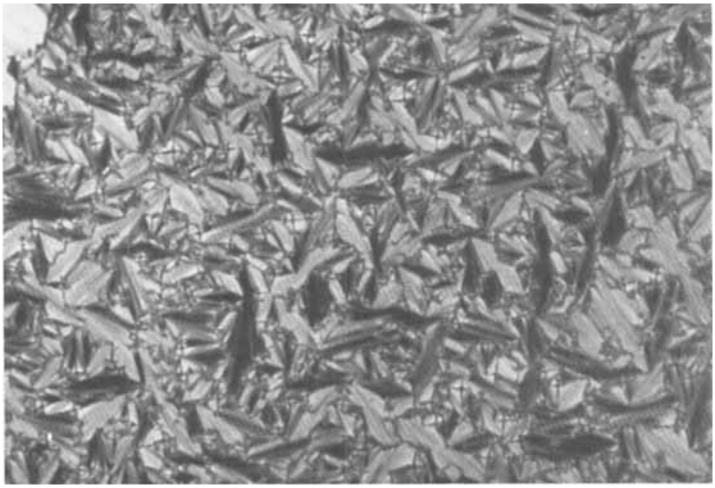


FIGURE 3 Complex **5**, S_A focal conic fan texture. Crossed polarizers, 180°C. See Color Plate XV.

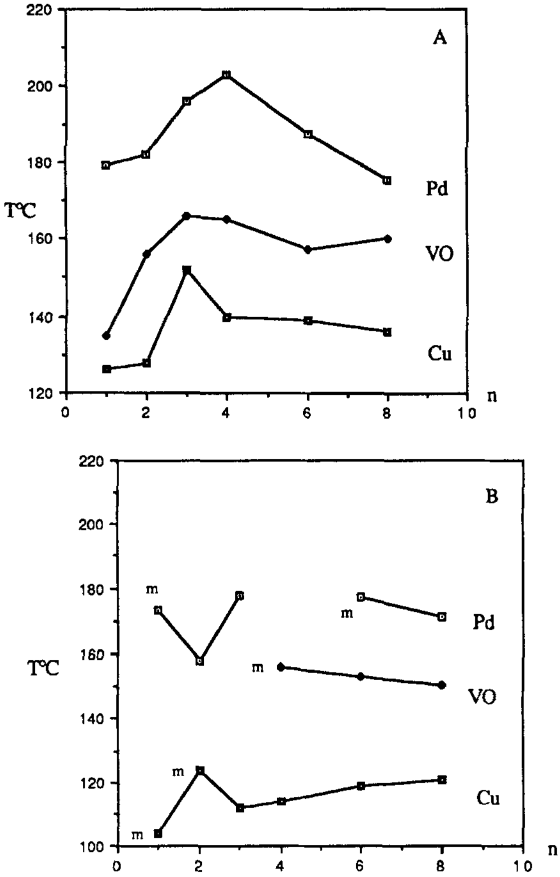


FIGURE 4 Plots of the clearing temperatures (A) and of the K–S_A temperatures (B) versus of the R_n alkyl chain length (n) for $(R_nL)_2M$ (M = Pd, VO and Cu) compounds (m = monotropic transition).

palladium complexes display the highest clearing temperatures both compared to copper and vanadyl series (Figure 4A).

As the mesomorphic behaviour is concerned, the copper compounds show smectic polimorphism (S_A, S_B and crystal smectic E phases) the vanadyl compounds S_A and S_C phases, while in the palladium compounds only S_A phases have been recognized. Such a mesophase is stable over a larger temperature range for copper(6a) than for palladium or vanadyl(6b) complexes and the temperature at which it appears follows again the order Cu(II) < VO(II) < Pd(II) (Figure 4B).

The molecular length of the investigated compounds depends on the alkoxy-chains laying on opposite sides of the molecule and not by the alkyl chains. As a consequence, the molecular length might be considered fairly constant along the series and approximately independent on the nature of the metal ion. The molecular length of these complexes, in their fully extended conformation, has been estimated to be about 42 Å. The experimental d_{SA} values for the three series of complexes are similar (Table II) and quite shorter with respect to the theoretical value. For the $(R_nL)_2Cu$ compounds such a result arises from a strong molecular interdigitation(21). In the present case too a similar model for the S_A phase could be invoked.

Concluding, with reference to the mesomorphism, the observed temperature trend, Cu(II) < VO(II) < Pd(II), suggests that for *N*-(4-dodecyloxysalicylidene)-4′-alkylanilines complexes intermolecular interactions are stronger in square planar Pd(II) species than in distorted square pyramidal VO(II) compounds, which in turn are stronger than in distorted square planar Cu(II) mesogens.

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