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Heteroligand Palladium Complexes with One or Two Chiral Centres

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Abstract A series of chiral mononuclear palladium(II) complexes, $[(Az_n)Pd(L_m)]$, **I-VIII**, have been synthesized. Herein the Az_nPd fragments represent the cyclopalladated 4-tetradecyloxy-4'-alkoxyazobenzene bearing an optically active carbon atom in a terminal alkoxy chain while HL_m is the anion arising from the achiral N-[4'-(dodecyloxy)resorcylidene]-4-(alkyl)anilines or the N-[4'-(dodecyloxy) resorcylidene]-4-(alkoxy)anilines containing a stereogenic center in a lateral chain. The optically active alkoxy tails are derived by S-(-)-β-citronellol and R-(-)-2-octanol.

Thermotropic mesomorphism, namely nematic and smectic phases, has been observed for almost all the complexes, with higher thermal stability and clearing temperatures of the same order or lower than those of the corresponding organic ligands.

Keywords Metallomesogens Palladium Azocompounds Resorcylideneamines Chiral centres

INTRODUCTION

The thermotropic metallomesogens form a quite new class of liquid crystalline compounds characterised by a molecular structure which contains at least one metal centre [1]. Many of them include a transition metal (e.g. Cr, Mn, Fe, Co, Ni, Cu, Zn, Rh, Pd, Ag, Re, Ir,

Pd, Pt, Au, Hg) [2] but examples with lanthanides are also known [3]. The synthesis of such species is usually performed starting from ligands having mesogenic characteristics and the product which results upon metal complexation may or may not retain the mesophases of the parent compounds. The generally observed trend is that the metalated species display more ordered mesophases than their respective ligands.

At present, the data concerning this point, although scattered, refer to complexes wherein only one mesogenic ligand is part of the molecular structure. Contrarily, as far as metallomesogens with two mesogenic ligands are concerned, no systematic studies have been reported. Since rules of thumb which correlate the thermotropism of a molecule which is organic in nature with that of its metalated derivative might be a useful tool to orientate the synthesis of materials with prefixed liquid crystalline properties, we have considered the case of compounds formed by two different and independent mesogenic entities connected together by a metal atom.

The palladium(II) ion gives stable tetracoordinated complexes featuring a square planar geometry. Accordingly, its derivatives with two thermotropic chelating ligands, adopt the expected structure with the two organic halves placed in a side by side arrangement. These are the compounds we have selected for this comparative study.

In previous reports we have shown that to prepare such palladium mesogens the organic species which meet best the requirements (e.g. palladium bonding ability, easy functionalization on the peripheral aliphatic chains to change the morphology of the mesophases and/or to insert a chiral group) are 4,4'-disubstituted azo/azoxybenzenes and

4,4'-disubstituted Shiff bases containing a salicylidene core [4-7]. As the azobenzene and the salicylidene molecular fragments display different chemistry, their treatment with a palladium(II) salt, in a two step reaction, is the only synthetic way which allows the preparation of mixed-ligand complexes [8].

In this paper we report the synthesis and characterization of two new series of chiral mononuclear cyclopalladated complexes, $[(Az_n)Pd(L_m)]$, **I-VIII**, obtained by reaction of 4-tetradecyloxy-4'-alkoxyazobenzenes bearing an optically active carbon atom in a terminal alkoxy chain with an appropriate Schiff base, namely the achiral N-[4'-(dodecyloxy)resorcylidene]-4-(alkyl)anilines or the N-[4'-(dodecyloxy) resorcylidene]-4-(alkoxy)anilines containing a stereogenic center in a lateral chain (Scheme 1). The chiral pools on both class of ligands are derived from the optically active alcohols S-(-)-β-citronellol (S-3,7-dimethyl-6-octen-1-ol) and R-(-)-2-octanol.

EXPERIMENTAL SECTION

Measurements.

The ^1H NMR spectra were recorded on a Bruker WH-300 spectrometer in $CDCl_3$ solution, with TMS as internal standard. Elemental analyses were performed with a Perkin-Elmer 2400 analyzer. The textures of the mesophases were studied with a Zeiss Axioscope polarizing microscope equipped with a Linkam C0 600 heating stage. The transition temperatures and enthalpies were measured on a Perkin-Elmer DSC-7 Differential Scanning Calorimeter with a heating and cooling rate of 10 °C/min. The apparatus was

calibrated with indium. Two or more heating/cooling cycles were performed on each sample.

The X-ray powder diffraction patterns were obtained by an INEL CPS120 powder diffractometer equipped with a position sensitive detector covering a scattering angle of 120°, with an angular revolution of 0.018°. Monochromatized CuKα radiation (λ= 1.54 Å) impinged on the ~ 1 mm thick sample, the temperature of which was controlled to ± 0.1° by a hot stage containing electrical resistors.

Synthesis

$[(Az_1)Pd(\mu\text{-}Cl)]_2$ [4] and HL_m [5,9] were synthesized as previously reported.

Synthesis of $[(Az_n)Pd(L_m)]$ complexes, **I-VIII**.

$[(Az_1)Pd(L_1)]$, **I**: a mixture of $[(Az_1)Pd(\mu\text{-}Cl)]_2$ (0,4 g, 0,3 mmol) and AgBF4 (0,1 g, 0,6 mmol) in acetonitrile (10 mL) was stirred at room temperature overnight, then filtered to remove the AgCl formed. The filtrate $[(Az_1)Pd(MeCN)_2][BF_4]$ was stripped to dryness, suspended in 10 ml of ethanol and added to an equimolar amount of HL_1. The mixture was stirred at room temperature for 2 days and then filtered. A brown solid was filtered off and purified by recrystallization from chloroform/ethanol to give the pure product in a 78% yield. Thermotropic behaviour in Table 1. Anal. Calcd for $C_{61}H_{91}N_3O_4Pd$: C, 70.66; H, 8.85; N, 4.05. Found: C, 70.49; H, 8.73; N, 4.17. ^1H NMR (300 MHz, $CDCl_3$) δ 7.96 (s, 1H, H^6), 7.89 (d, 2H, $H^{15,15'}$), 7.69 (d, 1H, H^{14}), 7.44 (d, 2H, $H^{7,7'}$), 7.20 (d, 2H, $H^{8,8'}$), 7.08 (d, 1H, H^5), 6.99 (d, 2H, $H^{16,16'}$), 6.51 (dd, 1H, H^{13}), 6.20 (s, 1H, H^4), 6.18 (s, 1H,

H^2), 5.32 (d, 1H, H^{12}), 4.06 (t, 2H, -OCH_2), 3.94 (t, 2H, -OCH_2), 3.70 (t, 1H, -OCH), 2.67 (m, 2H, -CH_2).

The homologous [(Az_n)Pd(L_m)] complexes were synthesized following the procedure described for [(Az_1)Pd(L_1)] reaction times (rt), colors, yields, NMR and IR data and elemental analyses are as follows.

[(Az_1)Pd(L_2)], II: RT: 2 days. Dark red. Yield 60 %. Thermotropic behaviour in Table 1. Anal. Calcd for $C_{67}H_{103}N_3O_4Pd$: C, 71.79; H, 9.26; N, 3.75. Found: C, 71.17; H, 9.11; N, 3.86. ^1H NMR (300 MHz, $CDCl_3$) δ 7.96 (s, 1H, H^6), 7.89 (d, 2H, $H^{15,15'}$), 7.69 (d, 1H, H^{14}), 7.42 (d, 2H, $H^{7,7'}$), 7.17 (d, 2H, $H^{8,8'}$), 7.08 (d, 1H, H^5), 6.98 (d, 2H, $H^{16,16'}$), 6.51 (dd, 1H, H^{13}), 6.20 (s, 1H, H^4), 6.17 (s, 1H, H^2), 5.31 (d, 1H, H^{12}), 4.06 (t, 2H, -OCH_2), 4.04 (t, 2H, -OCH_2), 3.36 (m, 1H, -OCH), 2.61 (m, 2H, -CH_2).

[(Az_1)Pd(L_3)], III: RT: 3 days. Red. Yield 40 %. Thermotropic behaviour in Table 1. Anal. Calcd for $C_{67}H_{103}N_3O_5Pd$: C, 70.78; H, 9.13; N, 3.69. Found: C, 69.90; H, 9.19; N, 3.50. ^1H NMR (300 MHz, $CDCl_3$) δ 7.94 (s, 1H, H^6), 7.89 (d, 2H, $H^{15,15'}$), 7.69 (d, 1H, H^{14}), 7.42 (d, 2H, $H^{7,7'}$), 7.07 (d, 1H, H^5), 6.99 (d, 2H, $H^{16,16'}$), 6.85 (d, 2H, $H^{8,8'}$), 6.52 (dd, 1H, H^{13}), 6.20 (s, 1H, H^4), 6.17 (s, 1H, H^2), 5.44 (d, 1H, H^{12}), 4.31 (m, 1H, -OCH), 4.06 (t, 2H, -OCH_2), 3.94 (t, 2H, -OCH_2), 3.79 (m, 1H, -OCH).

[(Az_1)Pd(L_4)], IV: RT: 5 days. Brown. Yield 60 %. Thermotropic behaviour in Table 1. Anal. Calcd for $C_{69}H_{105}N_3O_5Pd$: C, 71.26; H, 9.10; N, 3.61. Found: C, 71.14; H, 9.15; N, 3.35. ^1H NMR (300 MHz, $CDCl_3$) δ 7.94 (s, 1H, H^6), 7.89 (d, 2H, $H^{15,15'}$), 7.69 (d, 1H, H^{14}), 7.42

(d, 2H, $H^{7,7'}$), 7.08 (d, 1H, H^5), 6.98 (d, 2H, $H^{16,16'}$), 6.87 (d, 2H, $H^{8,8'}$), 6.54 (dd, 1H, H^{13}), 6.20 (s, 1H, H^4), 6.17 (s, 1H, H^2), 5.34 (d, 1H, H^{12}), 5.11 (m, 1H, CH=C), 4.06 (t, 2H, $-OCH_2$), 3.96 (t, 4H, $-OCH_2$), 3.40 (t, 1H, -OCH).

[(Az_2)Pd(L_1)], V: RT: 3 days. Brown. Yield 70 %. Thermotropic behaviour in Table 1. Anal. Calcd for $C_{63}H_{93}N_3O_4Pd$: C, 71.19; H, 8.82; N, 3.95. Found: C, 70.55; H, 8.71; N, 3.96. ^1H NMR (300 MHz, $CDCl_3$) δ 7.97 (s, 1H, H^6), 7.91 (d, 2H, $H^{15,15'}$), 7.66 (d, 1H, H^{14}), 7.44 (d, 2H, $H^{7,7'}$), 7.19 (d, 2H, $H^{8,8'}$), 7.08 (d, 1H, H^5), 6.99 (d, 2H, $H^{16,16'}$), 6.53 (dd, 1H, H^{13}), 6.21 (s, 1H, H^4), 6.18 (s, 1H, H^2), 5.31 (d, 1H, H^{12}), 5.12 (m, 1H, CH=C), 4.06 (t, 2H, $-OCH_2$), 3.95 (t, 2H, $-OCH_2$), 3.39 (t, 2H, $-OCH_2$), 2.67 (m, 2H, $-CH_2$).

[(Az_2)Pd(L_2)], VI: RT: 3 days. Dark red. Yield 73 %. Thermotropic behaviour in Table 1. Anal. Calcd for $C_{69}H_{104}N_3O_4Pd$: C, 72.32; H, 9.15; N, 3.67. Found: C, 72.13; H, 9.33; N, 3.69. ^1H NMR (300 MHz, $CDCl_3$) δ 7.96 (s, 1H, H^6), 7.91 (d, 2H, $H^{15,15'}$), 7.69 (d, 1H, H^{14}), 7.42 (d, 2H, $H^{7,7'}$), 7.16 (d, 2H, $H^{8,8'}$), 7.08 (d, 1H, H^5), 6.99 (d, 2H, $H^{16,16'}$), 6.52 (dd, 1H, H^{13}), 6.21 (s, 1H, H^4), 6.17 (s, 1H, H^2), 5.32 (d, 1H, H^{12}), 5.12 (m, 1H, CH=C), 4.06 (t, 2H, $-OCH_2$), 3.94 (t, 2H, $-OCH_2$), 3.38 (t, 2H, $-OCH_2$), 2.61 (m, 2H, $-CH_2$).

[(Az_2)Pd(L_4)], VII: RT: 3 days. Dark red. Yield 60 %. Thermotropic behaviour in Table 1. Anal. Calcd for $C_{71}H_{107}N_3O_5Pd$: C, 71.72; H, 9.07; N, 3.532. Found: C, 71.51; H, 9.24; N, 3.29. ^1H NMR (300 MHz, $CDCl_3$) δ 7.95 (s, 1H, H^6), 7.91 (d, 2H, $H^{15,15'}$), 7.70 (d, 1H, H^{14}), 7.42 (d, 2H, $H^{7,7'}$), 7.07 (d, 1H, H^5), 6.99 (d, 2H, $H^{16,16'}$), 6.87 (d, 2H, $H^{8,8'}$), 6.54 (dd, 1H, H^{13}), 6.21 (s, 1H, H^4), 6.18 (s, 1H,

H^2), 5.34 (d, 1H, H^{12}), 5.12 (m, 1H, CH=C), 4.08 (t, 2H, $-OCH_2$), 3.98 (t, 4H, $-OCH_2$), 3.42 (m, 2H, $-OCH_2$).

[$(Az_2)Pd(L_3)$], VIII: RT: 3 days. Brown. Yield 62 %. Thermotropic behaviour in Table 1. Anal. Calcd for $C_{69}H_{102}N_3O_5Pd$: C, 71.44; H, 8.86; N, 3.62. Found: C, 71.37; H, 9.21; N, 3.20. ^1H NMR (300 MHz, $CDCl_3$) δ 7.95 (s, 1H, H^6), 7.91 (d, 2H, $H^{15,15'}$), 7.70 (d, 1H, H^{14}), 7.42 (d, 2H, $H^{7,7'}$), 7.08 (d, 1H, H^5), 6.99 (d, 2H, $H^{16,16'}$), 6.84 (d, 2H, $H^{8,8'}$), 6.54 (dd, 1H, H^{13}), 6.21 (s, 1H, H^4), 6.17 (s, 1H, H^2), 5.39 (d, 1H, H^{12}), 5.12 (m, 1H, CH=C), 4.32 (m, 2H, $-OCH_2$), 4.06 (m, 2H, $-OCH_2$), 3.94 (t, 2H, $-OCH_2$), 3.43 (m, 1H, -OCH).

RESULTS AND DISCUSSION

Synthesis.

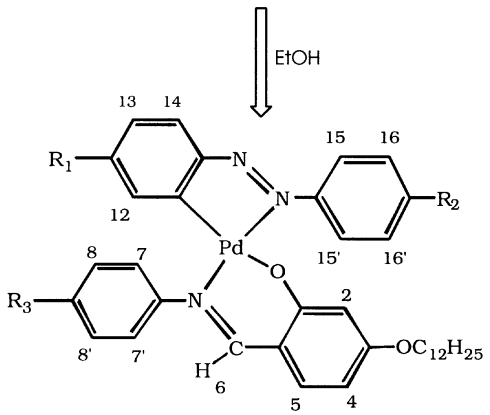
The synthesis of the mononuclear mixed-ligands $[(Az_n)Pd(L_m)]$ complexes **I-VII** has been accomplished according to the two step reaction pathway (Scheme 1) previously tested for the preparation of analogous $[(Azoxy)Pd(L_m)]$ compounds containing a cyclopalladated azoxy moiety and a chelating salicylideneaniline [8].

The dinuclear cyclopalladated chloro-bridged azobenzene precursors $[(Az_n)Pd(\mu\text{-}Cl)\}_2$ were first reacted with two equivalents of silver tetrafluoroborate in acetonitrile to give the corresponding solvato species $[(Az_n)Pd(MeCN)_2][BF_4]$. The intermediates were then reacted with an equimolar amount of the appropriate N-[4'-(dodecyloxy)resorcylidene]-4-(alkyl,alkoxy)-anilines HL_m, to afford the desired mononuclear products $[(Az_n)Pd(L_m)]$. The complexes **I-VIII** were characterized by elemental analyses and ^1H N.M.R.

spectroscopy (Experimental). These experimental data were in agreement with the expected stoichiometry confirming the presence of the only N,N-*trans* isomers whose molecular structures are proposed in Scheme 1.

$$[(Az_n)Pd(\mu\text{-}Cl)\}_2 + 2\,AgBF_4 \xrightarrow{MeCN} [(Az_n)Pd(MeCN)_2][BF_4]$$

$$[(Az_n)Pd(MeCN)_2][BF_4] + HL_m$$



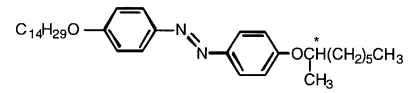
Compound	R_1	R_2	R_3
$[Az_1PdL_1]$, I	$OC_{14}H_{29}$	R(-)-2-octyl	C_2H_5
$[Az_1PdL_2]$, II	$OC_{14}H_{29}$	R(-)-2-octyl	C_8H_{17}
$[Az_1PdL_3]$, III	$OC_{14}H_{29}$	R(-)-2-octyl	R(-)-2-octyl
$[Az_1PdL_4]$, IV	$OC_{14}H_{29}$	R(-)-2-octyl	S(-)-β-citronellyl
$[Az_2PdL_1]$, V	$OC_{14}H_{29}$	S(-)-β-citronellyl	C_2H_5
$[Az_2PdL_2]$, VI	$OC_{14}H_{29}$	S(-)-β-citronellyl	C_8H_{17}
$[Az_2PdL_4]$, VII	$OC_{14}H_{29}$	S(-)-β-citronellyl	S(-)-β-citronellyl
$[Az_2PdL_3]$, VIII	$OC_{14}H_{29}$	S(-)-β-citronellyl	R(-)-2-octyl

SCHEME 1. Synthesis and proton numbering scheme for $[(Az_n)Pd(L_m)]$ complexes, **I-VIII**.

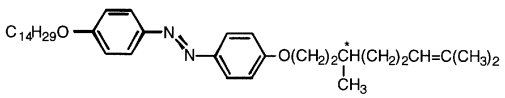
Mesomorphic Properties.

The uncomplexed HAz_n and HL_m ligands are liquid crystals which

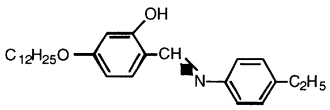
give smectic A/C or nematic and smectic mesophases, except for HAz_3, which does not exhibit mesomorphism at all; the previously investigated mesomorphic properties of these ligands are summarized in Chart 1.



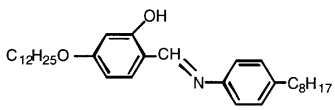
HAz_1 **Cr** 47 °C **I**



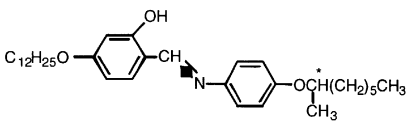
HAz_2 **Cr** 58 °C **SmA** 64 °C **I**



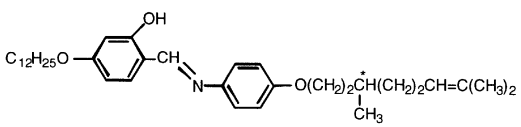
HL_1 **Cr** 59 °C **SmA** 63 °C **N** 78 °C **I**



HL_2 **Cr** 45 °C **SmC** 93 °C **SmA** 101 °C **I**



HL_3 **Cr** 47 °C **SmC*** 48 °C **I**



HL_4 **Cr** 50 °C **SmC*** 77 °C **I**

CHART 1. Stucture and mesomorphism of the HAz_n and HL_m ligands (Cr = Crystal; N = Nematic; Sm = Smectic, I = Isotropic).

TABLE 1. Optical and thermal properties of the $[(Az_n)Pd(L_m)]$ complexes.

COMPLEX	TRANSITION [a]	T[°C]	ΔH[KJmol^{-1}]
I	Cr-Cr'	60.7	28.4
	Cr'-I	80.9[b]	3.5
	I-SmA	79.0	4.1
	SmA-Cr	< - 30.0	
II	Cr-SmA	59.6	17.5
	SmA-I	84.8	7.4
	I-SmA	81.9	6.3
	SmA-Cr	< - 30.0	
III	Cr-I	64.1[b]	38.4
	I-N*	46.5	2.3
	N*-SmC*	39.3	0.4
	SmC*-Cr	12.5	3.1
IV	Cr-SmF*,G*	55.8	2.0
	SmF*,G*-I	64.5	7.1
	I-SmF*,G*	64.2	2.5
	SmF*,G*-Cr	< - 30.0	
V	Cr-Cr'	86.4	0.6
	Cr'-I	90.9 [b]	10.0
	I-SmA	88.1	4.9
	SmA-Cr	< - 30.0	
VI	Cr-SmC*	85.5	24.2
	SmC*-SmA	89.9	0.2
	SmA-I	99.9	6.5
	I-SmA	96.9	7.0
	SmA-SmC*	85.0	0.1
	SmC*-Cr	< - 30.0	
VII	Cr-SmC*	67.1	33.1
	SmC*-N*	76.7	1.8
	N*-I	82.6	2.1
	I-N*	79.7	2.5
	N*-SmC*	73.4	1.0
	SmC*-Cr	< - 30.0	
VIII	Cr-I	80.0	

[a] Cr: Crystal; Sm: smectic; N: Nematic; I: isotropic liquid
[b] Monotropic transition.

The thermal behaviour of complexes **I-VIII** was investigated by combining polarized optical microscope, differential scanning calorimetry and variable temperature low angle X-ray diffraction measurements. The nature of the mesophases, the transition temperatures and the corresponding enthalpy changes are reported in Table 1.

All the $[(Az_n)Pd(L_m)]$ complexes show mesomorphism featured by smectic and/or nematic phases, except compound **VIII,** which melts directly to an isotropic liquid at 80 °C. Moreover, a crystal to crystal transition is observed for both the complexes **I** and **V**. The nematic phases display a schlieren texture while the cholesteric N* exhibit the typical oily streaked textures. The smectic A phases show the characteristic fan-shaped textures and the chiral smectic C display the typical broken focal-conical ones.

The mesomorphism of complexes **I-VIII** will be discussed considering two homologous series wherein different combinations of a 4-tetradecyloxy-4'-alkoxyazobenzene HAz_n with N-(4-(dodecyloxy)salicylidene)-4'-alkyl,alkoxy-anilines differing in the nature or length of the terminal subtituents, are considered.

In particular, regarding the $[(Az_1)Pd(L_m)]$ series, containing the R-(-)-2-octyl group as the terminal tail in the azobenzene moiety, the metal complexation in all cases promotes the mesomorphism absent in the azobenzene HAz_1 precursor. In particular, $[(Az_1)Pd(L_1)]$ and $[(Az_1)Pd(L_2)]$ retain only the SmA phase of their achiral Schiff base parents HL_m, loosing the nematic (HL_1) and SmC (HL_2) character. For both complexes **I** and **II**, monotropic and enantiotropic, respectively, with clearing temperatures of about 80 °C, on cooling from the

isotropic liquid, the SmA remains stable until – 30 °C. Thus, with reference to their Schiff base precursors, the metal complexation widely broadens the mesomorphic range.

The presence of a further optically active centre incorporated in the alkoxy substituent in the resorcylideneaniline structure, induces a change in the mesomorphism from SmA to chiral N* and SmC* (**III**) or SmF*,G* (**IV**) and a remarkable decrease in the clearing points. In particular, compound **III,** bearing two identical chiral chains (R-(-)-2-octyloxy) on different aromatic rings, exhibits a monotropic cholesteric N* phase which, on cooling from the isotropic liquid, appears at 46 °C and, on further cooling, trasforms at 39 °C into a SmC* phase which persists until 12 °C. Interestingly, when the stereogenic centres arise from different chiral alcohols (S-(-)-β-citronellyloxy on the Schiff base), complex **IV** shows an enantiotropic tilted smectic F or G phase, between 56 and 64 °C.

With respect to the HL_3 precursors, **III** shows the same SmC* phase, enriched by the N* one, but stable over a rather broader range of temperature, while for **IV** the SmC* phase observed in the HL_5 ligand becomes a more ordered chiral SmF*,G* phase, with a clearing temperature lower by 13 °C which, on cooling from the isotropic liquid, persists until –30 °C.

Comparisons of compounds $[(Az_l)Pd(L_m)]$ with their azo precursors reavel, for the R-(-)-2-octanol derivatives, **I-IV**, a general trend related to the molecular structure; there is an increase in entropy on going from the uncomplexed ligand 4-[R-(-)-2-octyloxy],4'-(tetradecyloxy)-azobenzene (not liquid crystal) to the mononuclear complexes **I**

(monotropic S_A phase), **II** (enantiotropic S_A phase) and **III** (SmC*, N*).

Finally, the [$(Az_2)Pd(L_m)$] series is characterised by the S-(-)-β-citronellyloxy as the terminal chain of the azoligand. Within this series, the liquid crystalline properties dramatically change as a function of the nature of the HL_m ligand. Thus, as regards complexes derived from achiral Schiff bases, containing only one optically active centre on the azobenzene structure: **V** displays a monotropic SmA phase, while **VI** shows, enantiotropically, the sequence SmC* (85 °C) SmA phase (90 °C). With respect to the uncomplexed ligands, **V** preserves the SmA of the corresponding parents, losing the N one of the Schiff base; on the contrary **VI** preserves the same sequence as the HL_m precursor and assumes a further smectogenic character (SmC*) with respect to HAz_n. Moreover, on cooling, both complexes remain liquid crystalline until - 30 °C, so the thermal stability range of the mesophase is remarkably similar for both complexes **V** and **VI** and very much higher than their organic ligands.

Finally, for complexes **VII** and **VIII,** whose molecular structures include an additional optically active centre on the Schiff base, the mesomorphic behaviour proves to be quite sensitive to changes in the chiral groups. In particular, compound **VII**, bearing two S-(-)-β-citronellyl as terminal chains, retains the SmC* phase of the HL_5 ligand at 85 °C, losing the more ordered SmA phase of the azo ligand precursor HAz_4 and instead having a cholesteric phase between 77 and 83 °C, which is absent in both the organic parents. On cooling down from the isotropic liquid the cholesteric phase reappears at 80 °C and, on further cooling, it trasforms into the SmC* which supercools until

– 30 °C. Interestingly, even if the clearing temperature is slightly increased, **VII** exhibits mesomorphism, on cooling, over a temperature range that is much wider than that for the uncomplexed ligands.

In contrast, the presence of two identical S-(-)-β-citronellyl groups in complex **VIII** affords a molecular structure that depresses the mesomorphic aptitude and **VIII** melts directely to an isotropic liquid at 80 °C.

X-ray Diffraction Measurements.

The nature of the different mesophases has been confirmed by variable temperature X-ray diffraction analysis. Table 2 reports, for all the investigated complexes, the periodicity, *d*, characteristic of the different mesophases (as obtained by the application of the Bragg law to the low angle peaks), together with the molecular length as estimated by molecular modeling (with the aliphatic chains in the all *trans* conformation). The quantity *d* gives the layer spacing in the smectic phase while in the nematic phase it corresponds to the average molecular length. A comparison between the values of *d* and *L* in the N and SmA phases shows that the layer spacing is, in any case, lower than the molecular length, indicating that the aliphatic chains are partially melted and folded. As regards the tilted smectic phases, the comparison between *d* and *L* allows us to estimate an upper limit of β = 31° (**III**) and 36° (**VII**) for the average tilt angle β in the SmC* phase. Finally, the diffraction pattern obtained for the $[(Az_1)Pd(L_4)]$ complex **IV**, indicates the presence of a lamellar phase with the molecules packed hexagonally in the smectic layers.

TABLE 2. X-ray diffraction data of the **[(Az$_n$)Pd(L$_m$)]** complexes.

COMPLEX	PHASE	d^a, Å	L^b, Å
I	SmA	31.1	38.2
II	SmA	33.7	38.2
III	SmC*	32.7	38.2
	N*	27.5	
IV	SmF*,G*	32.4	38.2
V	SmA	32.1	39.5
VI	SmA	32.9	39.5
VII	SmC*	32.1	39.5
	N*	30.8	

[a] Layer spacing derived from diffraction patterns (in the central region of phases stability).

[b] Molecular length determined by molecular modeling (aliphatic chains in all *trans* conformation).

From the comparison of d and L values it has been possible to conclude that this smectic phase is a tilted one ($\beta = 32°$) but, as the difference between the two possible tilted smectic chiral F* and G* phases is not possible to define, the identification for **IV** is left ambigous.

CONCLUSIONS

The complexation of palladium(II) to different calamitic moieties, namely chiral 4-tetradecyloxy-4'-alkoxyazobenzenes HAz$_n$ and achiral N-[4'-(dodecyloxy)resorcylidene]-4-(alkyl)anilines or chiral N-[4'-

(dodecyloxy) resorcylidene]-4-(alkoxy)anilines HL_m allows the synthesis of a new series of mixed-ligand complexes, $[(Az_n)Pd(L_m)]$ containing one or two stereogenic centres located in the aliphatic chains. Almost all these complexes show mesomorphism (N and Smectic phases) whose properties are affected by the length of the terminal chains and by the number and type of chiral centres. A comparison of the thermal behaviour of compounds **I-VIII** with respect to the corresponding organic ligands is summarized in Table 3.

TABLE 3. Optical and thermal properties of the **$[(Az_n)Pd(L_m)]$** complexes and of the corresponding organic ligands.

Complexes	HAz_n	HL_m	$[(Az_n)Pd(L_m)]$
I	**Cr** 47 **I**	**Cr** 59 **SmA** 63 **N 78 I** **I** 78 **N** 60 **SmA** 47 **Cr**	**Cr** 61 **Cr'** 81 **I** **I** 79 **SmA** < -30 **Cr**
II	**Cr** 47 **I**	**Cr** 45 **SmC** 93 **SmA** 101 **I** **I** 101 **SmA** 93 **SmC** 45 **Cr**	**Cr** 60 **SmA** 85 **I** **I** 82 **SmA** < -30 **Cr**
III	**Cr** 47 **I**	**Cr** 47 **SmC*** 48 **I** **I** 48 **SmC*** 30 **Cr**	**Cr** 64 **I** **I** 46 **N*** 39 **SmC*** 12 **Cr**
IV	**Cr** 47 **I**	**Cr** 50 **SmC*** 77 **I** **I** 74 **SmC*** 44 **Cr**	**Cr** 56 **SmF*,G*** 64 **I** **I** 64 **SmF*,G*** < -30 **Cr**
V	**Cr** 58 **SmA** 64 **I** **I** 64 **SmA** 46 **Cr**	**Cr** 59 **SmA** 63 **N** 78 **I** **I** 78 **N** 60 **SmA** 47 **Cr**	**Cr** 86 **Cr'** 91 **I** **I** 88 **SmA** < -30 **Cr**
VI	**Cr** 58 **SmA** 64 **I** **I** 64 **SmA** 46 **Cr**	**Cr** 45 **SmC** 93 **SmA** 101 **I** **I** 101 **SmA** 93 **SmC** 45 **Cr**	**Cr** 85 **SmC*** 90 **SmA** 100 **I** **I** 97 **SmA** 85 **SmC*** < -30 **Cr**
VII	**Cr** 58 **SmA** 64 **I** **I** 64 **SmA** 46 **Cr**	**Cr** 50 **SmC*** 77 **I** **I** 74 **SmC*** 44 **Cr**	**Cr** 67 **SmC*** 77 **N*** 83 **I** **I** 80 **N*** 73 **SmC*** < -30 **Cr**
VIII	**Cr** 58 **SmA** 64 **I** **I** 64 **SmA** 46 **Cr**	**Cr** 47 **SmC*** 48 **I** **I** 48 **SmC*** 30 **Cr**	**Cr** 80 **I**

The monochiral complexes **I-II** and **V-VI**, with the optically active centre on the azobenzene precursor, all exhibit the SmA. The length of the terminal chain in the Schiff base ligand determines the stability of

the mesophase; the shortest homologues ($R_3 = C_2H_5$) show monotropic behaviour (**I** and **V**) while the longest behave enantiotropically and, in the case of compound **VI** (R_2 = (S-(-)-β-citronellyl), it causes a more odered, chiral mesophase (SmC*) to appear. Among the dichiral complexes **III-IV** and **VII-VIII**, remarkable changes occur depending on whether the chiral fragments located in the azobenzene and on the Schiff bases are the same or not. The presence of two identical chiral groups determines a N*-SmC* sequence of phases, monotropic for the 2-octanol derivative (**III**) and enantiotropic for the S-(-)-β-citronellol one (**VII**). Besides, the introduction of two different chiral groups depresses the mesomorphic aptitude and implies a more ordered phase for complex **IV** or a lack of liquid crystallinty for **VIII**.

In conclusion, in order to tailor species whose mesomorphic properties are modulated by means different functionalization sites [10,11], a series of liquid crystalline oligomers characterised by two different calamitic moieties connected through a metal atom have been prepared. A comparison of the newly synthetised mononuclear metallomesogens $[(Az_n)Pd(L_m)]$ with the corresponding organic precursors shows that this cyclopalladated molecular structure i) generally promotes the appearance of new and more ordered phases, ii) in dichiral complexes with identical chiral groups it gives rise to nematogenitiy, iii) despite the usual trend for metallomesogens, the clearing temperatures are of the same order or lower than those of the corresponding organic ligand and the complexes **I-VIII** have an enhanced thermal stability, on cooling being stable until – 30 °C.

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