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Cyclopalladated Azo- and Azoxybenzene Mononuclear Complexes Containing a Chiral Chelating Ligand

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Chiral metallomesogens are materials of great interest for different technological applications. In most of the reported chiral liquid crystals, the chiral centre is located remote from the central core of the molecule. Our goal is to prepare new chiral metallomesogens featuring the stereogenic centre as close to the metal ion as possible. Accordingly, new mononuclear cyclopalladated complexes based on azo or azoxybenzene ligands (4,4′-bis(octyloxybenzoyloxy)azobenzene, **HAzoCOO-8***, p-azoxyanisole,* **HAzoxy***, 4,4′-bis(hexyloxy)azobenzene,* **HAzo-6***, or 4,4′-bis(hexyloxy)azoxybenzene,* **HAzoxy-6***) containing the chiral chelating ligand (D-(−)-α-Phenylglycinol,* **H(Phenylgly)***) have been synthesized and fully characterized. ^{1}H NMR spectra of the azoxybenzene cyclopalladated complexes show the presence of just one isomer while those of the products obtained from the azobenzene ligands evidence the formation of isomeric mixtures. Nematic mesophases have been observed for complexes* **[(AzoCOO-8)Pd(Phenylgly)]** *and* **[(Azoxy-6)Pd-(Phenylgly)]**. *Mixtures of* **HAzoCOO-8** *and the corresponding cyclopalladated complex,* **[(AzoCOO-8)Pd(Phenylgly)]***, in different molar ratios, have been prepared in order to promote the development of chiral mesophases.*

Keywords: azocompounds; chiral mesophases; cyclopalladation; metallomesogens

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INTRODUCTION

In the last years metal-containing liquid crystals (metallomesogens) have attracted a lot of attention since they are materials which combine the properties exhibited by convectional liquid crystals, such as fluidity, physical anisotropy and response to external electric and magnetic fields, with the properties (i.e., redox or magnetic, for instance) due to the presence of the metal centre [1–9].

Cu(II), Ni(II), Pt(II) or Pd(II) are interesting as metal centres for the synthesis of metallomesogens since the flat molecular structure of mesogenic ligands is retained in the square-planar complexes after coordination, thus the structural anisotropy necessary for the formation of the mesophase is not destroyed. One effective way to obtain organometallic complexes is through reaction of cyclometalation with organic compounds containing an aromatic C−H bond and a heteroatom in an appropriate position [10]. Azobenzene and azo derivatives were the first species shown to undergo palladation and a variety of metallomesogens based on cyclopalladated azobenzenes have been reported [11,12]. On the other hand, introduction of chirality in metallomesogens provides materials very attractive for technological applications since they can exhibit properties such as ferroelectricity, photorefractivity or nonlinear optical response [9,13].

In particular, previous investigations proved that cyclopalladated azobenzene complexes are remarkable photorefractive materials [14]. Photorefractivity is a property exhibited by some materials in which the redistribution in space of photogenerated charges induce a nonuniform electric space-charge field which can affect the refractive index of the material [15]. Mesophases are attractive for photorefractivity because of their high spontaneous birefringence and the wide variety of field-induced refractive index control mechanisms [16]. In general the liquid crystalline phase is not intrinsically photoconducting, so that the use of a dopant is necessary in order to achieve the space-charge field set up.

Recently, the first example of a mesomorphic material that exhibits photorefractive behaviour without any doping has been described [17]. Interestingly, this material consists of a mononuclear palladium(II) complex containing a cyclopalladated alkoxyazobenzene and a substituted salicylaldimine, both bearing a stereogenic centre in their terminal chains. In this complex, as well as in most of the reported chiral liquid crystals, the chiral centre is remote from the molecular central core, while the presence of the chiral centre close to the metal centre is supposed to provide materials with higher Ps values and therefore good photorefractive properties.

In this article we report, as an extension of the previous investigations, the synthesis, characterization and thermal behaviour of new cyclopalladated azo- and azoxybenzene mononuclear complexes with a chiral O,N chelating ligand, the D-(–)-α-phenylglycinol, selected in order to obtain new materials exhibiting chiral mesophases and photorefractive behaviour.

EXPERIMENTAL SECTION

Measurements

The ^{1}H NMR spectra were recorded on a Bruker Avance AC-300 spectrometer in $CDCl_3$ or DMSO-d^6 solution, using tetramethylsilane (TMS) as internal standard. Elemental analyses (CHN) were performed with a Perkin Elmer 2400 microanalyzer by the Microanalytical Laboratory at the University of Calabria. Infrared spectra (KBr) were recorded on a Perkin Elmer Spectrum One. The textures of the mesophases were studied with a Zeiss Axioscope polarizing microscope equipped with a Linkam C0 600 heating stage. The transition temperatures were measured on a Perkin-Elmer DSC-7 Differential Scanning Calorimeter with a heating and cooling rate of 10°C/min. The instrument was calibrated with Indium.

Synthesis

All chemicals and the commercially available $PdCl_2$ (Aldrich), $AgBF_4$ (Aldrich), 1,3-dicyclohexylcarbodiimide (Aldrich), 4-pyrrolidinopyridine (Aldrich), 4-(hexyloxy)aniline (Aldrich), 4,4′-bis(hexyloxy)azoxybenzene (Eastman Kodak), H(Azoxy-6), 4-*n*-octyloxybenzoic acid (Aldrich), *p*-azoxyanisole (Aldrich), H(Azoxy), 4-nitrophenol (Fluka A.G.) and D-(–)-α-phenylglycinol (Fluka A.G.) were used without further purification.

4,4′-Dihydroxyazobenzene [18], $[Pd(PhCN)_2Cl_2]$ [19], 4,4′-bis(hexyloxy) azobenzene, H(Azo-6) [20], $[(Azoxy)Pd(\mu\text{-}Cl)]_2$ [21], $[(Azoxy\text{-}6)Pd(\mu\text{-}Cl)]_2$ [21,22], $[(Azo\text{-}6)Pd\ (\mu\text{-}Cl)]_2$ [20], $[(Azoxy)Pd\text{-}9(MeCN)_2]BF_4$ [21] and $[(Azo\text{-}6)Pd(MeCN)_2]BF_4$ [22] were prepared as described in the literature.

Synthesis of 4,4′-Bis(octyloxybenzoyloxy)azobenzene (HAzoCOO-8)

A mixture of 4,4′-dihydroxyazobenzene (0.80 g, 3.73 mmol), 4-*n*-octyloxybenzoic acid (1.87 g, 7.46 mmol), 1,3-dicyclohexylcarbodiimide (1.69 g, 8.21 mmol) and 4-pyrrolidinopyridine (0.11 g, 0.75 mmol) in 80 mL of dichloromethane, was stirred at room temperature for 4 days.

The grey solid formed was filtered off and the solution washed with distilled water, a 5% CH_3COOH solution and again with distilled water. The organic phase was dried over anhydrous Na_2SO_4 and the solvent removed under reduced pressure. The resulting orange solid was recrystallized from dichloromethane/diethyl ether to give a yellow solid. Yield: 53%. Anal. Calcd for $C_{42}H_{50}N_2O_6$ (Mw = 678.86): C 74.31 H 7.42 N 4.13. Found C 73.81 H 7.38 N 4.06%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.16 (d, $J = 8.9$ Hz, 4H), 8.01 (d, $J = 8.9$ Hz, 4H), 7.38 (d, $J = 8.9$ Hz, 4H), 6.98 (d, $J = 8.9$ Hz, 4H), 4.05 (t, $J = 6.6$ Hz, 4H), 1.75–1.90 (m, 4H), 1.20–1.50 (m, 20H), 0.90 (t, $J = 6.9$ Hz, 6H). IR (KBr, υ/cm^{-1}): 2926, 2854 ($-CH_2-$), 1740, 1730 (COO).

Synthesis of [(AzoCOO-8)Pd(μ-Cl)]$_2$

To a stirred suspension of HAzoCOO-8 (0.30 g, 0.44 mmol) in 18 mL of MeOH, $[Pd(PhCN)_2Cl_2]$ (0.17 g, 0.44 mmol) dissolved in 18 mL of toluene was added. The resulting suspension was stirred under reflux for 2 days. Once at room temperature the solid was filtered and washed with MeOH and Et_2O. The solid was then dissolved in chloroform and filtered over celite. The solvent was evaporated and the resulting orange solid vacuum dried. Yield: 40%. Anal. Calcd for $C_{84}H_{98}Cl_2N_4O_{12}Pd_2$ (Mw = 1638.76): C 61.57 H 5.98 N 3.42. Found C 61.02 H 6.08 N 3.23%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.09 (d, $J = 8.9$ Hz, 2H), 8.07 (d, $J = 8.9$ Hz, 2H), 7.92 (br d, 1H), 7.90 (d, $J = 8.3$ Hz, 2H), 7.35 (br d, 2H), 7.17 (br s, 1H), 7.12 (dd, $J_1 = 8.3$ Hz, $J_2 = 2.3$ Hz, 1H), 6.93 (d, $J = 8.9$ Hz, 2H), 6.89 (d, $J =$ 8.9, 2H), 4.03 (t, $J = 6.6$ Hz, 2H), 3.96 (t, $J = 6.6$ Hz, 2H), 1.90–1.75 (m, 4H), 1.55–1.20 (m, 20H), 0.90 (t, $J = 6.5$ Hz, 6H). IR (KBr, υ/cm^{-1}): 2925, 2855 ($-CH_2-$), 1732 (COO).

Synthesis of [(AzoCOO-8)Pd(Phenylgly)]

The binuclear complex [(AzoCOO-8)Pd(μ-Cl)]$_2$ (0.25 g, 0.15 mmol) was dissolved in 30 mL of hot dichloromethane. The solution was allowed to cool to room temperature and then $AgBF_4$ (0.058 g, 0.30 mmol) was added. After stirring in the darkness for 18 h the suspension was filtered over celite. To the resulting orange solution, D-(–)-α-phenylglycinate potassium salt (0.026 g, 0.15 mmol), previously prepared by reacting equimolar amounts of D-(–)-α-phenylglycinol and KOH in EtOH at room temperature for 1 day and recrystallizing from $CHCl_3/Et_2O$, was added. The colour of the solution immediately turned to dark orange. After stirring at room temperature for 4 days, the solution was washed several times with distilled water, the organic phase dried over anhydrous Na_2SO_4, filtered and the solvent evaporated under reduced pressure. The crude was then dissolved in

dichloromethane and filtered over celite. The solvent was partially evaporated and addition of hexane afforded a dark red solid which was filtered, washed with hexane and vacuum dried. Yield: 63%. Anal. Calcd for $C_{50}H_{59}N_3O_7Pd$ (Mw = 919.97): C 65.28 H 6.41 N 4.56. Found C 64.94 H 6.74 N 4.92%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.20–8.10 (m), 7.97 (d, J = 8.2 Hz), 7.92 (d, J = 8.4 Hz), 7.50 (d, J = 7.8 Hz), 7.44 (d, J = 8.2 Hz), 7.40–7.10 (m), 7.06 (d, J = 8.8 Hz), 7.02 (br s), 6.98–6.83 (br s), 6.76 (d, J = 8.7 Hz), 6.65 (d, J = 8.5), 6.46 (br s), 4.20–3.70 (m), 2.16 (br s), 2.03 (br s), 1.92–1.70 (m), 1.68–1.20 (m), 0.91 (m). IR (KBr, υ/cm^{-1}): 3287, 3239, 3065 (NH), 2927, 2856 ($-CH_2-$), 1730 (COO).

Synthesis of [(Azoxy-6)Pd(Phenylgly)]

To a suspension of [(Azoxy-6)Pd(MeCN)$_2$]BF_4 (0.45 g, 0.67 mmol) in 20 mL EtOH, D-(–)-α-phenylglycinol (0.091 g, 0.67 mmol) and K_2CO_3 (0.091 g, 0.67 mmol) were added. The reaction mixture was stirred for 2 days at room temperature and then filtered over celite. After evaporating the solvent, the residual solid was dissolved in CH_2Cl_2 and washed several times with water. The organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated in vacuum. Addition of hexane gave rise to an orange solid which was filtered and vacuum dried. Yield: 65%. Anal. Calcd for $C_{32}H_{43}N_3O_4Pd$ (Mw = 639.82): C 60.07 H 6.72 N 6.56. Found C 59.85 H 6.69 N 6.92%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 (d, J = 9.0 Hz, 1H), 7.45–7.26 (m, 6H), 7.25–7.20 (m, 1H), 7.11 (d, J = 2.6 Hz, 1H), 6.93 (d, J = 9.0 Hz, 2H), 6.69 (dd, J_1 = 8.8 Hz, J_2 = 2.6 Hz, 1H), 4.18–4.05 (m, 4H), 3.95 (br t, 3H), 2.66 (br t, 1H), 2.43 (br d, 1H), 1.90–1.65 (m, 4H), 1.55–1.20 (m, 12 H), 0.98–0.80 (m, 6H). IR (KBr, υ/cm^{-1}): 3300, 3061 (NH), 2930, 2858 ($-CH_2-$).

Synthesis of [(Azo-6)Pd(Phenylgly)]

This complex was synthesized following the procedure described for [(Azoxy-6)Pd(Phenylgly)], by reacting [(Azo-6)Pd(MeCN)$_2$]BF_4 with D-(–)-α-phenylglycinol in the presence of K_2CO_3. Orange solid. Yield: 82%. Anal. Calcd for $C_{32}H_{43}N_3O_3Pd$ (Mw = 623.77): C 61.62 H 6.89 N 6.73. Found C 61.20 H 6.93 N 6.84%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.34 (br d, 2H), 7.73 (d, J = 8.8 Hz, 2H), 7.46–7.13 (m, 12H), 6.99 (br s, 1H), 6.89 (d, J = 9.2 Hz, 2H), 6.85 (d, J = 9.1 Hz, 2H), 6.68 (dd, J_1 = 8.2 Hz, J_2 = 2.5 Hz, 1H), 6.59 (dd, J_1 = 8.2 Hz, J_2 = 2.4 Hz, 1H), 6.35 (br s, 1H), 4.76 (br s, 1H), 4.30 (br s, 1H), 4.22–3.98, 3.96, 3.95 (m, t, t, 10H), 3.88–3.68 (m, 2H), 3.13 (br s, 1H), 2.79 (br s, 1H), 1.98–1.55 (m, 16H), 1.52–1.03 (m, 24H), 0.88 (m, 12H). IR (KBr, υ/cm^{-1}): 3061 (NH), 2953, 2930, 2857 ($-CH_2-$).

Synthesis of [(Azoxy)Pd(Phenylgly)]

This complex was synthesized following the procedure described for [(Azoxy-6)Pd(Phenylgly)], by reacting equimolar amounts of [(Azoxy)Pd(MeCN)$_2$]BF_4, D-(–)-α-phenylglycinol and K_2CO_3. The crude product was recrystallized from CH_2Cl_2/heptane. Orange solid. Yield: 60%. Anal. Calcd for $C_{22}H_{23}N_3O_4Pd$ (Mw = 499.64): C 52.88 H 4.60 N 8.40; found C 52.76 H 4.98 N 8.25%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 (d, J = 8.8 Hz, 1H), 7.40–7.20 (m, 7H), 7.13 (d, J = 2.6 Hz, 1H), 6.94 (d, J = 9.0 Hz, 2H), 6.69 (dd, J_1 = 9.0 Hz, J_2 = 2.6 Hz, 1H), 4.18–4.02 (m, 2H), 4.00–3.80, 3.90, 3.81 (m, s, s, 7H), 2.73 (br t, 1H), 2.48 (br d, 1H). IR (KBr, υ/cm^{-1}): 3060 (NH), 2953, 2930, 2857 (–CH_2–).

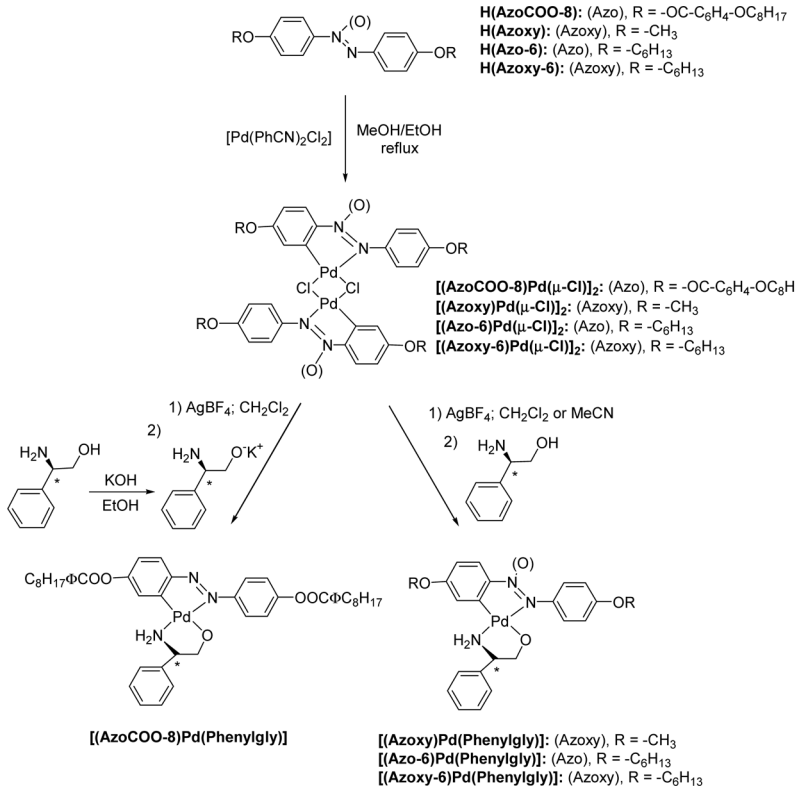
RESULTS AND DISCUSSION

Synthesis

The dinuclear chloro-bridged complexes or their ionic derivative formed by treatment with a silver salt, are convenient starting materials for the synthesis of mononuclear complexes by reaction with chelating monoanionic ligands [21–26]. These new mononuclear cyclopalladated complexes containing the D-(–)-α-phenylglycinol O,N chelating ligand were prepared reacting the dinuclear chloro-bridged complexes with $AgBF_4$ in acetonitrile, except for the [(AzoCOO-8)Pd(CH_2Cl_2)$_2$]BF_4, which was prepared in dichloromethane due to the insolubility of [(AzoCOO-8)Pd(μ-Cl)]$_2$ in acetonitrile.

[(Azo-6)Pd(Phenylgly)], [(Azoxy)Pd(Phenylgly)] and [(Azoxy-6)Pd(Phenylgly)] were obtained by reaction of the corresponding tetrafluoroborate intermediates with D-(–)-α-phenylglycinol in the presence of K_2CO_3. However, attempts to obtain the [(AzoCOO-8)Pd-(Phenylgly)] complex in this way were unfruitful, being finally successfully achieved by first transforming the D-(–)-α-phenylglycinol into its potassium salt by reaction with KOH in ethanol. General synthesis of the complexes is shown in Scheme 1.

According to the ^{1}H NMR spectra, only one specie was formed in the case of [(Azoxy)Pd(Phenylgly)] and [(Azoxy-6)Pd(Phenylgly)], while for [(AzoCOO-8)Pd(Phenylgly)] and [(Azo-6)Pd(Phenylgly)] isomeric mixtures were obtained as a result of a coordination N,N-*trans* or N,N-*cis* of the anionic D-(–)-α-phenylglycinol ligand in the mononuclear complex (isomeric ratio difficult to elucidate for the former and about 1:1 molar ratio for the latter, which ^{1}H NMR spectrum is shown in Fig. 1). Taking into account these results, also observed previously in similar complexes [26], the presence of an oxigen atom on one nitrogen of the azo group leads in some way to the coordination of the monoanionic N,O chelating ligand in a preferred position; therefore, it



SCHEME 1 General synthesis of the complexes.

seems to be more appropriate the use of azoxybenzene derivatives in order to avoid the generation of isomeric mixtures.

Representative examples of the ^{1}H NMR spectra are reported for complexes [(Azoxy-6)Pd(Phenylgly)] and [(Azo-6)Pd(Phenylgly)] (Fig. 1). In particular, for [(Azo-6)Pd(Phenylgly)] it results that signals corresponding to the protons closer to the cyclopalladate ring (H-3 and H-4,4′) are remarkably shifted in one isomer with respect to the other as evidenced by the $\Delta\delta$ of 0.94 and 0.64 ppm observed for the H-4,4′ and H-3 protons, respectively. Moreover, aromatic protons of the phenylglycinol ligand appear as multiplets in the region between 7.40 and 7.20 ppm while a large chemical shift (not shown in Fig. 1) is also observed for the signals corresponding to the NH_2 protons which appear as broad signals at 4.76 and 4.30 ppm for one isomer and at 3.13 and 2.79 ppm for the other one. However, it should be pointed out that from the ^{1}H NMR spectra it was not possible to find out which signals correspond to which isomer or if the preferred configuration is N,N-*cis* or N,N-*trans*.

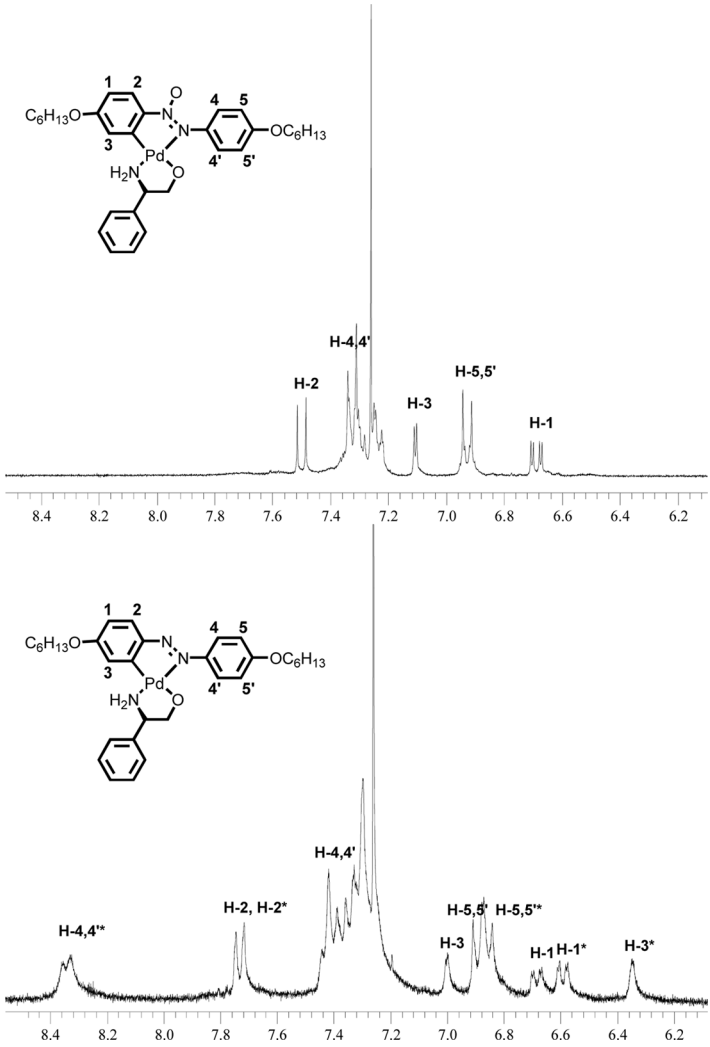


FIGURE 1 Aromatic region of the ^{1}H NMR spectra of complexes [(Axoxy-6)Pd(Phenylgly)] and [(Azo-6)Pd(Phenylgly)] and proton numering.

Thermal Behaviour

Thermal properties of the ligands as well as the binuclear and mononuclear complexes have been studied by polarized optical microscopy and DSC (Table 1).

The H(Azoxy), H(Azoxy-6) and H(Azo-6) ligands show an enantiotropic nematic phase while H(AzoCOO-8), on heating, melts to the

TABLE 1 Thermal Properties of the Ligands and the Corresponding *Ortho*-Palladated Complexes

Compound	Phases and transition temperatures (°C)
Ligand	
H(Azoxy)	K 120 N 137 I
H(Azoxy-6)	K 80 N 126 I
H(Azo-6)	K 104 N 116 I
H(AzoCOO-8)	K 135 SmC 160 N 312 I
Binuclear complex	
[(Azoxy)Pd(μ-Cl)]$_2$	K 350 dec
[(Azoxy-6)Pd(μ-Cl)]$_2$	K 298 dec
[(Azo-6)Pd(μ-Cl)]$_2$	K 190 N 220 I
[(AzoCOO-8)Pd(μ-Cl)]$_2$	K 230 N 290 deC
Mononuclear chiral complex	
[(Azoxy)Pd(phenylgly)]	K 140 dec
[(Azoxy-6)Pd(phenylgly)]	K 129 N 130 I dec
[(Azo-6)Pd(phenylgly)]	K 130 I dec
[(AzoCOO-8)Pd(phenylgly)]	K 150 N 225 I dec

K: Crystal; N: Nematic; Sm: Smectic; I: isotropic liquid; dec: decomposition.

SmC mesophase at 135°C followed by the nematic one at 160°C, which persists until the clearing point (312°C): The same sequence of phases has been restored on cooling from the isotropic state: the nematic phase, which appears at 312°C is stable until 144°C when the SmC phase which remained until solidification at 120°C.

The transition temperatures for the binuclear chloro-bridged complexes are remarkably higher. In particular, [(Azoxy)Pd(μ-Cl)]$_2$ and [(Azoxy-6)Pd(μ-Cl)]$_2$ decompose before clearing while [(Azo-6)Pd(μ-Cl)]$_2$ and [(AzoCOO-8)Pd(μ-Cl)]$_2$ show a nematic phase between 190 and 220°C and between 285 and 290°C, respectively.

The mononuclear chiral complexes, [(Azoxy)Pd(Phenylgly)] and [(Azo-6)Pd(Phenylgly)] do not display mesomorphism and decompose at temperatures between 130°C and 140°C (Table 1). For complex [(Azoxy-6)Pd(Phenylgly)] a tendency to develop a nematic mesophase is observed when the compound melts to the isotropic liquid but in the mean time it partially decomposes, preventing further investigations during the cooling cycle. The complex containing the longer azobenzene ligand, [(AzoCOO-8)Pd(Phenylgly)], shows a schlieren texture, corresponding to a nematic mesophase, from 150°C to 225°C where it melts together with a partial decomposition. Because of the [(Azoxy-6)Pd(Phenylgly)] and [(AzoCOO-8)Pd(Phenylgly)] partial decomposition, cooling down from the isotropic liquid some transitions

are observed. Thus, the DSC trace of [(Azoxy)Pd(Phenylgly)] shows the peak of crystallization at $T_{onset} = 84^{\circ}C$ and for [(Azoxy-6)Pd(Phenylgly)] a nematic texture, in some regions of the sample, appears at 85°C and crystallization takes place at 50°C.

Since chiral mesophases have not been observed in any case, mixtures of the ligand H(AzoCOO-8) with the corresponding chiral complex [(AzoCOO-8)Pd(Phenylgly)] have been prepared in order to achieve SmC^* or N^* materials, that is, to use the chiral complex as dopant to promote chirality in the SmC and N mesophases observed in H(AzoCOO-8). In particular, mixtures containing a 5%, 10%, 25%, and 50% molar ratio of the mononuclear complex have been prepared from $CHCl_3$ solutions. Thermal behaviour of the mixture containing a 5% of chiral complex is almost the same to that observed for neat H(AzoCOO-8), developing a SmC mesophase between 137°C and 165°C and then a nematic phase until melting to the isotropic liquid at 315°C. During the first cooling the nematic mesophase appears from 311°C to 149°C, temperature at which becomes SmC until crystallization takes place at 120°C. In the second cooling process, it is possible to observe, between 170°C and 143°C, a texture (not identified) that could be associated to a chiral mesophase. A similar

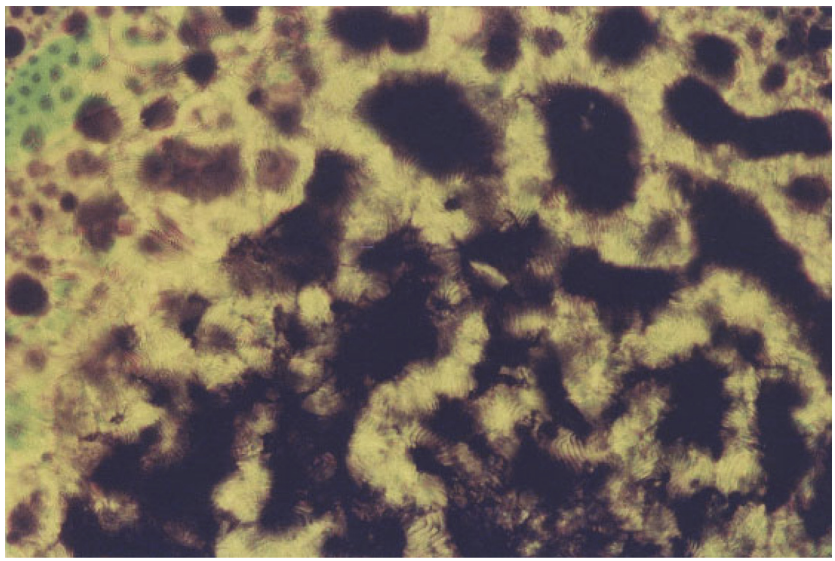


FIGURE 2 Texture of the N^* mesophase of the mixture H(AzoCOO-8):[(AzoCOO-8)Pd(Phenylgly)] 1:1 observed through crossed polarizers at 202°C on cooling. (See COLOR PLATE III)

texture is observed in the first cooling between 250°C and 147°C in the mixture containing a 10% of the complex and between 240°C and 147°C for that containing a 25%. Differently, the 50% mixture displays a mesophase above 135°C which was not identified since a typical texture was not developed however, when the temperature is increased over 168°C, a N^* mesophase is observed (Fig. 2) and remains until 204°C when isotropization is observed.

CONCLUSIONS

Some new cyclopalladated mononuclear complexes with a chiral centre close to the metal ion have been synthesized. Isomeric mixtures derived from a coordination N,N-*cis*or N,N-*trans* of the monoanionic D-(–)-α-phenylgflycinol chelating ligand were obtained in the case of cyclopalladated azobenzene complexes while just one isomer is formed when azoxybenzene ligands are used. Interestingly, a 1:1 mixture of the ligand H(AzoCOO-8) and of the pertinent complex [(AzoCOO-8) Pd(phenylgly)] is found to develop a N^* mesophase.

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