## Transition metals complexed in ordered mesophases. XV. Synthesis, characterization and mesomorphic properties of new potentially ferroelectric liquid crystals: Acetylacetonate *p,p'*-dialkoxyazobenzene mononuclear palladium(II) complexes

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# Transition metals complexed in ordered mesophases

## XV†. Synthesis, characterization and mesomorphic properties of new potentially ferroelectric liquid crystals: Acetylacetonate *p,p'*-dialkoxyazobenzene mononuclear palladium(II) complexes

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The sysnthesis and characterization of two series of chiral mononuclear palladium(II) azocompounds, $(L_N(n))Pd(acac)]$, prepared by bridge splitting reactions or the dinuclear parents $\{Pd[L_N(n)]\mu\text{-}Cl)\}_2$ with thallium acetylacetonate are reported. All the complexes, bearing a stereogenic centre in the alkoxy lateral chain ($R^*O = R\text{-}(-)\text{-}2\text{-}octyl$; $S\text{-}(-)\text{-}\beta\text{-}citronellyl$), are mesomorphic. Their thermotropic behaviour has been investigated by differential scanning calorimetry, optical microscopy and X-ray diffraction. Worthy of note, the clearing temperatures of all the compounds are below 70°C. The relationship between ligands, $\mu$-Cl dimers and mononuclear acetylacetonate complexes is discussed.

## 1. Introduction

The synthesis of new liquid crystalline materials containing palladium atoms as a part of the rigid molecular core has been recently extended to species formed by chiral ligands [2–4]. In particular, with reference to compounds wherein chirality resides in a terminal alkoxy chain, we recently reported on both Schiffs base [2] and azocomplexes [3] of general formula $L_2Pd$ and $L_2Pd_2$, respectively. These complexes are featured by an 'H-shaped' molecular geometry and display disordered smectic phases (A and C*) with transition temperatures over 100°C. On the other hand, it has been shown that organometallic species whose molecules include, together with a

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mesogenic ligand ($L$), the palladium acetylacetonate fragment, i.e. $L$Pd(acac), display melting and clearing temperatures lower than those of the corresponding $L_2$Pd$_2$ or $L_2$Pd species [5–7]. Such a behaviour has been explained in terms of molecular asymmetry which gives rise to a 'P-shaped' geometry able to create the appropriate molecular disorder [8]. Accordingly, in order to obtain chiral metallo-mesogens which exhibit $S_C^*$ phases over a broad temperature range around room temperature, the two series of chiral mononuclear compounds, $[L_N(n)$Pd(acac)], where $L_N(n)$ are azobenzene ligands bearing in the 4- and 4'-positions $C_nH_{2n+1}O$ ($n = 7$, 10, 12, 14) and $R^*O$ ($R^* = R$-($-$)-2-octyl, $N = 1$ or $S$-($-$)-$\beta$-citronellyl, $N = 2$) groups respectively, have been studied.

In this we report on the synthesis and thermotropic behaviour of the series **1(n)** and **2(n)** investigated by optical microscopy, differential scanning calorimetry (DSC) and X-ray diffraction.

## 2. Experimental

### 2.1. *Measurements*

The investigation and characterization of the mesophases have been performed by DSC, optical microscopy and X-ray powder diffraction. The optical observations have been made, using a Zeiss Axioskop polarizing microscope equipped with a Linkam CO 600 heating stage. Transition temperatures and enthalpies were determined using a Perkin–Elmer DSC-7 differential scanning calorimeter. Finally, X-ray diffraction measurements have been made using the INEL CPS 120 powder diffractometer equipped with a position sensitive detector covering 120° in the scattering angle $2\theta$, with an angular resolution of 0·018° in $\theta$. Ge(101) monochromatized CuK$\alpha$ radiation ($\lambda = 1\cdot54$ Å) collimated with an appropriate slit system, was used. The samples, $\sim 1$ mm thick, were placed between two thin Al sheets, fixed to a circular hole (1 cm diameter) in an Al sample holder. Heating was achieved by a hot stage whose control stability was $\pm 0\cdot1$°C.

### 2.2. *Synthesis*

All commercially available starting materials, $R$-($-$)-2-octanol (Fluka, A.G., 98 per cent optical purity) and $S$-($-$)-$\beta$-Citronellol ($S$-3,7-dimethyloct-6-en-1-ol) (>99 per cent optical purity) were used without further purification. The complexes thallium acetylacetonate, [Tl(acac)], and $\{$Pd$[L_n(N)](\mu$-Cl)$\}_2$ were prepared according to [9] and [3] respectively.

### 2.2.1. *Synthesis of the $[L_N(n)$Pd(acac)] complexes **1(n)** and **2(n)***

The complexes **1(n)** and **2(n)** were prepared according to the following procedure: to a suspension of $\{$Pd$[L_N(n)](\mu$-Cl)$\}_2$ (0·14 mmol) in ethanol (15 ml), 2 equivalents of [Tl(acac) (0·28 mmol) were added and the mixture was refluxed under nitrogen for 2 h; a black insoluble residue was filtered off and the filtrate cooled to 0°C. The brown precipitate which formed was filtered off and washed with water and ethanol. Thermal data are given in the table. Colours, meling points, $^1$H NMR data, elemental analysis results and yields for the $[L_N(n)$Pd(acac)] complexes, **1(n)** and **2(n)**, are given below:

$[L_1(7)$Pd(acac)], **1(7)**: brown solid; $^1$H, NMR (300 MHz, CDCl$_3$): isomer A, $\delta$: 4·10 (t, 2 H, OCH$_2$), 4·42 (m, 1 H, OCH), 5·41 (s, 1 H, H$^{11}$), 6·71 (m, 1 H, H$^1$), 6·91 (dd, 2 H, H$^{6,8}$), 7·00 (d, 1 H, H$^3$), 7·76 (d, 1 H, H$^2$), 7·99 (d, 2 H, H$^{5,7}$); isomer **B**, $\delta$: 4·02 (t, 2 H, OCH$_2$), 4·54 (m, 1 H, OCH); between isomer **A** and **B** no differences

involving the aromatic signals were detected. Elemental analysis (per cent): Calculated for $C_{32}H_{46}N_2O_4Pd$: C, 61·09; H, 7·37; N, 4·45. Found: C, 60·77; H, 7·36; N, 4·01 per cent. Yield 76 per cent.

[$L_1$(10)Pd(acac)], **1(10)**: brown solid; $^1H$ NMR (300 MHz, CDCl$_3$): isomer **A**, $\delta$: 4·10 (t, 2 H, OCH$_2$), 4·44 (m, 1 H, OCH), 5·41 (s, 1 H, H$^{11}$), 6·71 (m, 1 H, H$^1$), 6·92 (dd, 2 H, H$^{6,8}$), 7·00 (d, 1 H, H$^3$), 7·76 (d, 1 H, H$^2$), 7·99 (d, 2 H, H$^{5,7}$); isomer **B**, $\delta$: 4·02 (t, 2 H, OCH$_2$), 4·55 (m, 1 H, OCH); between isomer **A** and **B** no differences involving the aromatic signals were detected. Elemental analysis (per cent): Calculated for $C_{35}H_{52}N_2O_4Pd$: C, 62·63; H, 7·81; N, 4·17. Found: C, 61·78; H, 8·14; N, 4·32 per cent. Yield 65 per cent.

[$L_1$(12)Pd(acac)], **1(12)**: brown solid; $^1H$ NMR (300 MHz, CDCl$_3$): isomer **A**, $\delta$: 4·09 (t, 2 H, OCH$_2$), 4·43 (m, 1 H, OCH), 5·41 (s, 1 H, H$^{11}$), 6·71 (m, 1 H, H$^1$), 6·91 (dd, 2 H, H$^{6,8}$), 7·00 (d, 1 H, H$^3$), 7·76 (d, 1 H, H$^2$), 7·99 (d, 2 H, H$^{5,7}$); isomer **B**, $\delta$: 4·02 (t, 2 H, OCH$_2$), 4·55 (m, 1 H, OCH); between isomer **A** and **B** no differences involving the aromatic signals were detected. Elemental analysis (per cent): Calculated for $C_{37}H_{56}N_2O_4Pd$: C, 63·55; H, 8·07; N, 4·01. Found: C, 63·41; H, 8·02; N, 4·11 per cent. Yield 70 per cent.

[$L_1$(14)Pd(acac)], **1(14)**: orange solid; $^1H$ NMR (300 MHz, CDCl$_3$): isomer **A**, $\delta$: 4·10 (t, 2 H, OCH$_2$), 4·45 (m, 1 H, OCH), 5·41 (s, 1 H, H$^{11}$), 6·71 (m, 1 H, H$^1$), 6·91 (dd, 2 H, H$^{6,8}$), 7·00 (d, 1 H, H$^3$), 7·77 (d, 1 H, H$^2$), 7·99 (d, 2 H, H$^{5,7}$); isomer **B**, $\delta$: 4·02 (t, 2 H, OCH$_2$), 4·55 (m, 1 H, OCH); between isomer **A** and **B** no differences involving the aromatic signals were detected. Elemental analysis (per cent): Calculated for $C_{39}H_{60}N_2O_4Pd$: C, 64·40; H, 8·31; N, 3·85. Found: C, 64·57; H, 8·31; N, 3·73 per cent. Yield 65 per cent.

[$L_2$(7)Pd(acac)], **2(7)**: brown solid; $^1H$ NMR (300 MHz, CDCl$_3$): isomers **(A + B)**, $\delta$: 4·01 (m, 4 H, OCH$_2$), 5·12 (m, 1 H, CH=C(CH$_3$)$_2$), 5·41 (s, 1 H, H$^{11}$), 6·72 (dd, 1 H, H$^1$), 6·96 (d, 2 H, H$^{6,8}$), 7·02 (br s, 1 H, H$^3$), 7·77 (d, 1 H, H$^2$), 8·01 (d, 2 H, H$^{5,7}$). Elemental analysis (per cent): Calculated for $C_{34}H_{48}N_2O_4Pd$: C, 62·33; H, 7·38: N, 4·27. Found: C, 62·66; H, 7·45; N, 4·42 per cent. Yield 68 per cent.

[$L_2$(10)Pd(acac)], **2(10)**: brown solid; $^1H$ NMR (300 MHz, CDCl$_3$): isomers **(A + B)**, $\delta$: 4·08 (m, 4 H, OCH$_2$), 5·12 (m, 1 H, CH=C(CH$_3$)$_2$), 5·41 (s, 1 H, H$^{11}$), 6·72 (dd, 1 H, H$^1$), 6·92 (d, 2 H, H$^{6,8}$), 7·01 (m, 1 H, H$^3$), 7·76 (d, 1 H, H$^2$), 8·00 (d, 2 H, H$^{5,7}$). Elemental analysis (per cent): Calculated for $C_{37}H_{54}N_2O_4Pd$: C, 63·74; H, 7·81: N, 4·02. Found: C, 64·10; H, 7·90; N, 4·25 per cent. Yield 75 per cent.

[$L_2$(12)Pd(acac)], **2(12)**: brown solid; $^1H$ NMR (300 MHz, CDCl$_3$): isomers **(A + B)**, $\delta$: 4·08 (m, 4 H, OCH$_2$), 5·12 (m, 1 H, CH=C(CH$_3$)$_2$), 5·41 (s, 1 H, H$^{11}$), 6·72 (dd, 1 H, H$^1$), 6·92 (d, 2 H, H$^{6,8}$), 7·01 m, 1 H, H$^3$), 7·76 (d, 1 H, H$^2$), 8·00 (d, 2 H, H$^{5,7}$). Elemental analysis (per cent): Calculated for $C_{39}H_{58}N_2O_4Pd$: C, 64·58; H, 8·06: N, 3·86. Found: C, 64·84; H, 8·15; N, 3·92 per cent. Yield 70 per cent.

[$L_2$(14)Pd(acac)], **2(14)**: brown solid; $^1H$ NMR (300 MHz, CDCl$_3$): isomers **(A + B)**, $\delta$: 4·08 (m, 4 H, OCH$_2$), 5·11 (m, 1 H, CH=C(CH$_3$)$_2$), 5·41 (s, 1 H, H$^{11}$), 6·72 (dd, 1 H, H$^1$), 6·93 (d, 2 H, H$^{6,8}$), 7·01 (m, 1 H, H$^3$), 7·76 (d, 1 H, H$^2$), 8·00 (d, 2 H, H$^{5,7}$). Elemental analysis (per cent): Calculated for $C_{41}H_{62}N_2O_4Pd$: C, 65·37; H, 8·29: N, 3·72. Found: C, 65·55; H, 8·26; N, 3·65 per cent. Yield 72 per cent.

## 3. Results and discussion

The synthesis of cyclopalladated mononuclear acetylacetonate complexes can be accomplished under mild conditions by treating cyclopalladated halo-bridged dinuclear compounds with thallium acetylacetonate [10, 11]. Thus, in the present case,
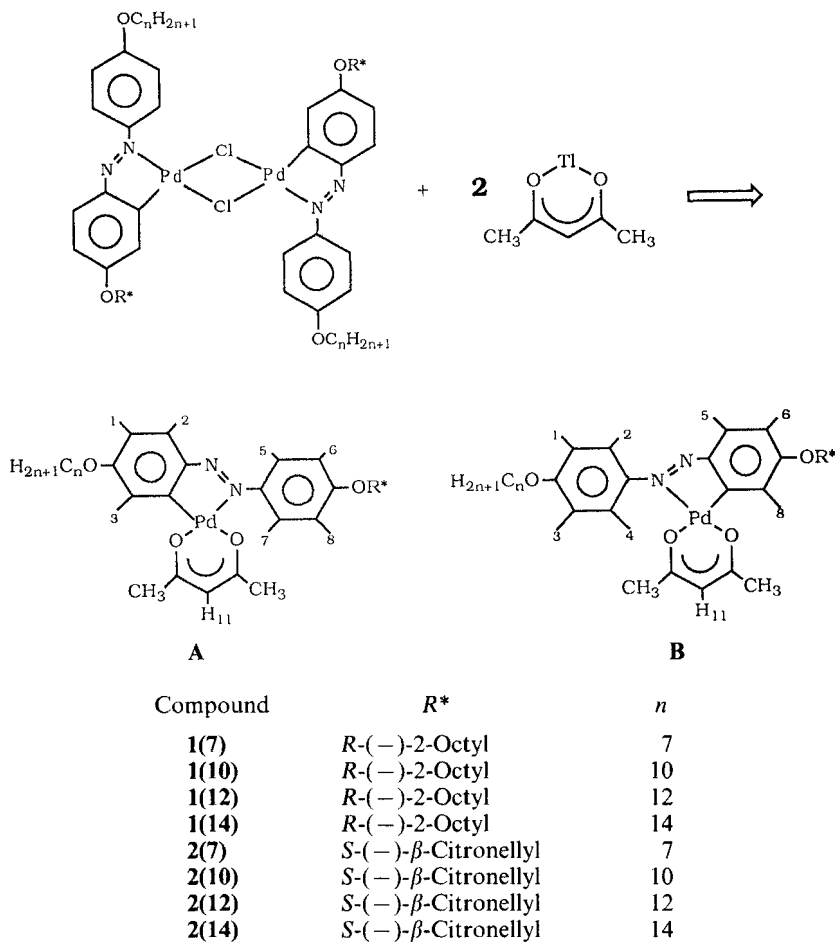
Scheme.   Synthesis of $[L_N(n)Pd(acac)]$ compounds, **1(n)** and **2(n)**, and general formulae with proton numbering schemes for the two complexes **A** and **B**.

| Compound | $R^*$ | $n$ |
|----------|-------|-----|
| **1(7)** | $R$-$(-)$-2-Octyl | 7 |
| **1(10)** | $R$-$(-)$-2-Octyl | 10 |
| **1(12)** | $R$-$(-)$-2-Octyl | 12 |
| **1(14)** | $R$-$(-)$-2-Octyl | 14 |
| **2(7)** | $S$-$(-)$-$\beta$-Citronellyl | 7 |
| **2(10)** | $S$-$(-)$-$\beta$-Citronellyl | 10 |
| **2(12)** | $S$-$(-)$-$\beta$-Citronellyl | 12 |
| **2(14)** | $S$-$(-)$-$\beta$-Citronellyl | 14 |

starting from the $\{Pd[L_N(n)](\mu\text{-Cl})\}_2$ species (see the scheme), the corresponding $[L_N(n)Pd(acac)]$ compounds are formed (see experimental).

However, these dinuclear compounds, prepared as previously described [3], actually are 1:1 mixtures of complexes which result from a non-selective palladation of the benzene rings bearing $C_nH_{2n+1}O$ or $R^*O$ groups [3]; therefore their derivatives too should be equimolar mixtures of the complexes **A** and **B** shown in the scheme. Indeed, $^1H$ NMR spectra of compounds containing the $R$-$(-)$-2-octyloxy substituent show separate signals for both the $-OCH^*(CH_3)-$ and $-OCH_2-$ groups, accounting for the presence of the **A** and **B** complexes in a 1:1 ratio.

All the synthesized compounds are mesomorphic. The liquid crystal transition temperatures, the nature of the mesophases, the transition enthalpies and the X-ray diffraction data are reported in the table.

Even though the corresponding dinuclear precursor is not mesomorphic, the shortest member of the series **1**, **1(7)**, exhibits an enantiotropic cholesteric phase—

Transition temperatures and enthalpy changes for the mesomorphic $[L_N(n)\text{Pd(acac)}]$ compounds†.

| Compound | Transition† | $T/°C$ | $\Delta H/\text{J g}^{-1}$ | $d‡/\text{Å}$ | $L§/\text{Å}$ |
|---|---|---|---|---|---|
| $[L_1(7)\text{Pd(acac)}]$ **1(7)** | C–Ch | 55·0 | | 29·4 (Ch) | 29·4 |
| | Ch–I | 58·5 | 41·6 | | |
| | I–Ch | 58·0 | | | |
| | Ch–C | 33·0 | | | |
| $[L_1(10)\text{Pd(acac)}]$ **1(10)** | C–I | 61·0 | 29·6 | | |
| | I–S$_C^*$ | 41·0 | | 31·8 (S$_C^*$) | 33·1 |
| | S$_C^*$–C | R.T. | | | |
| $[L_1(12)\text{Pd(acac)}]$ **1(12)** | C–I$^b$ | 43·0 | | | |
| | I–S$_A^b$ | 43·0 | | 31·4 (S$_A$) | 35·7 |
| | S$_A$–K$^b$ | R.T. | | | |
| $[L_1(14)\text{Pd(acac)}]$ **1(14)** | C–I | 55·8 | 63·5 | | |
| | I–S$_C^*$ | 44·0 | | 33·6 (S$_C^*$) | 38·2 |
| | S$_C^*$–C | R.T. | | | |
| $[L_2(7)\text{Pd(acac)}]$ **2(7)** | C–Ch | 47·2 | 22·3 | 27·2 (Ch) | 30·7 |
| | Ch–I | 65·1 | 1·3 | | |
| | I–Ch | 64·7 | 1·3 | | |
| | Ch–C | 40·0 | | | |
| $[L_2(10)\text{Pd(acac)}]$ **2(10)** | C–S$_A$ | 41·0 | 1·6 | 30·4 (S$_A$) | 34·5 |
| | S$_A$–Ch | 59·6 | 2·2 | 30·6 (Ch) | |
| | Ch–I | 66·0 | 2·1 | | |
| | I–Ch | 64·2 | 1·6 | | |
| | Ch–S$_A$ | 58·1 | | | |
| | S$_A$–C | 35·0 | | | |
| $[L_2(12)\text{Pd(acac)}]$ **2(12)** | C–S$_A$ | 40·0 | 6·8 | 32·8 (S$_A$) | 37·0 |
| | S$_A$–I | 63·1 | 7·2 | | |
| | I–S$_A$ | 61·9 | | | |
| | S$_A$–C | 35·0 | | | |
| $[L_2(14)\text{Pd(acac)}]$ **2(14)** | C–S$_A$ | 48·0 | 7·2 | 34·0 (S$_A$) | 39·5 |
| | S$_A$–I | 60·8 | 7·5 | | |
| | I–S$_A$ | 60·6 | | | |
| | S$_A$–C | 36·0 | | | |

†C, crystal; S, smectic; Ch, cholesteric; I, isotropic liquid.

‡Layer spacing in the smectic phases derived from diffraction patterns (at the mid-point of the phase's temperature range). For the cholesteric phases, $d$ gives the average molecular length.

§Molecular length theoretically estimated (alkyl chains in all *trans*-conformation).

3°C range—before clearing at 58·5°C. With a very slow cooling rate ($0·1°\text{C min}^{-1}$) from the isotropic liquid, the same mesophase appears at 58°C and remains stable until 33°C when the Ch–C transition is observed. On increasing the alkoxy chain length (**1(10)**, **1(12)**, **1(14)**), the compounds assume smectogenic character and preserve the same, monotropic, phases of the chloro-bridged parents [2], but with wider ranges of temperature and lower clearing points by about 60°C. In particular, on cooling from the isotropic liquid, the S$_C^*$ phase (with the typical broken focal-conical texture) appears at 41°C for **1(10)** and at 44°C for the **1(14)** complex. The values of the tilt angles calculated from the experimental X-ray diffraction data

and the theoretically estimated molecular lengths are 16 and 28°, respectively, for the two compounds. Finally, compound **1(12)** exhibits a monotropic $S_A$ phase at 43°C and is capable of supercooling to room temperature. It is noteworthy that all the mononuclear complexes **1(n)** exhibit mesomorphism, although none of the $HL_1(n)$ ligands forms a liquid crystal [2].

As in the series **1(n)**, the clearing temperatures of the members of series **2(n)** are below 70°C. In detail, **2(7)** shows an enantiotropic cholesteric phase and its thermal stability range extends from 47°C to 65°C. Compound **2(10)** exhibits two liquid crystalline phases: a disordered $S_A$ phase at 41°C and a cholesteric phase (with a typical oily streaked texture) between 59°C and 66°C. On cooling down from the isotropic liquid, a cholesteric phase appears at 64°C and, on further cooling, transforms at 58°C into a $S_A$ phase which persists down to room temperature. An enantiotropic $S_A$ phase, showing the typical focal conical texture, is observed for **2(12)** at 40°C and for **2(14)** at 48°C before clearing occurs at 63°C and 60°C respectively. In both cases, the smectic A phase obtained on cooling from the isotropic liquid persists until room temperature. However, the thermal stability range of the mesophase (about 20°C) is remarkably similar for all the **2(n)** compounds.

With respect to the $\{Pd[L_2(n)](\mu\text{-}Cl)\}_2$ parent compounds [3], the melting and clearing temperatures of the **2(n)** series are about 100°C lower, as shown in figure 1, where the transition temperatures are plotted against $n$. Furthermore, by comparing the mesomorphic behaviour, it can be shown that the shorter chain members of the series, **2(7)** and **2(10)**, exhibit an enantiotropic cholesteric phase instead of the smectic C* phase, while the longer chain members, **2(12)** and **2(14)**, preserve the enantiotropic $S_A$ phase of the binuclear parents. Moreover, with reference to the
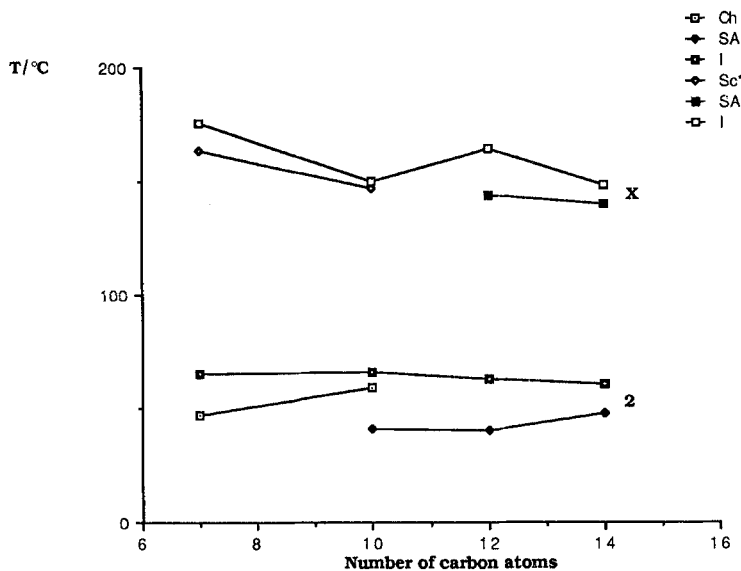


Figure 1. Plots of mesomorphic transition temperatures versus the $C_nH_{2n+1}O$ chain length ($n$) for complexes $\{Pd[L_2(n)](\mu\text{-}Cl)\}_2$, (**X**) and $[L_2(n)]Pd(acac)]$, (**2**), Symbols represent transitions to the phase indicated on heating.

corresponding $HL_2(n)$ ligands, the derivatives **2(n)** exhibit the same phases over wider ranges of temperature and with very similar clearing temperature.

As an example of the mesomorphic behaviour of the compounds, figure 2 reports the X-ray diffraction spectra measured at different temperatures during a complete thermal cycle for compound **2(10)**. The figure clearly shows the sharp peak in the small angle region (see (*b*) and (*f*)) associated with the Bragg reflection from the smectic layers, while the weak diffuse low angle peak in (*c*) and (*e*) is characteristic of the nematic-like short range order in the cholesteric phase.

The species containing $\beta$-citronellyl as the chiral group, i.e. $HL_2(n)$, $\{Pd[L_2(n)]\mu\text{-}Cl)\}_2$ and **2(n)**, are all mesomorphic and, at least for the $S_A$ mesophase, by comparing the ratio between the experimental layer spacing (*d*) and the calculated molecular length (*L*), it is possible to assess the different molecular packings they adopt.
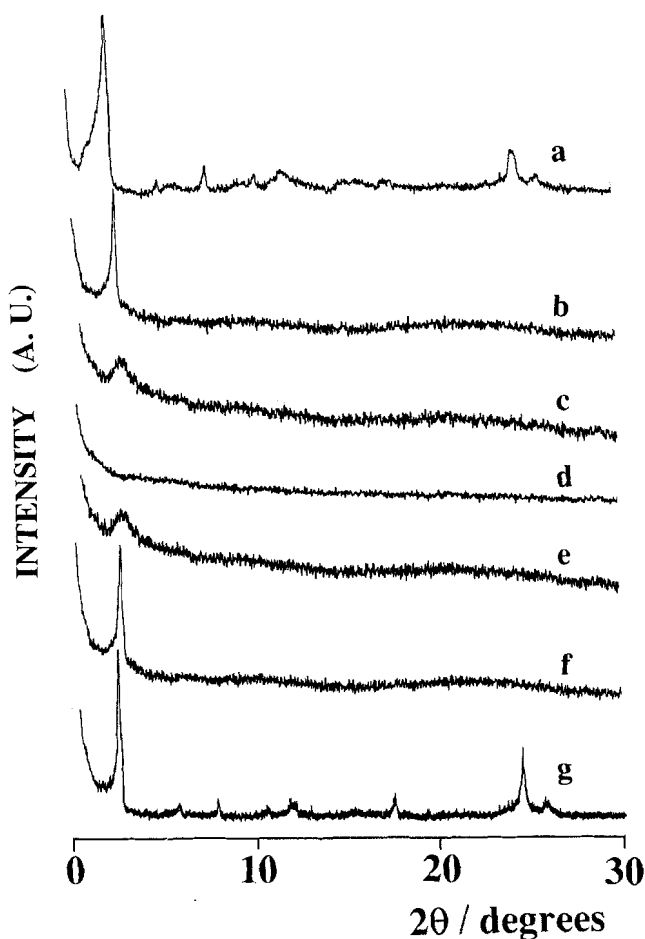


Figure 2.   X-ray diffraction patterns of compound **2(10)** measured at different temperatures between room temperature and the isotropization temperature during a complete thermal cycle. Heating cycle: (*a*) $T = 27°C$; (*b*) $T = 50°C$; (*c*) $T = 63°C$; (*d*) $T = 66°C$. Cooling cycle: (*e*) $T = 61°C$; (*f*) $T = 50°C$; (*g*) $T = 27°C$.

The ligands $HL_2(n)$ give values of the ratio $d/L$ which vary between $\sim 1$ and $0.9$ (the typical range for monolayer $S_A$ phases), whereas, for $\{Pd[L_2(n)]\mu\text{-Cl}\}_2$, the ratio $d/L$ ranges between $0.68$ and $0.86$ [3]. Thus, for the binuclear complexes, a model where the aliphatic chains are partially melted and folded or where the chains appear strongly interdigitated has to be invoked for the structural conformation. The $d/L$ data arising from the present investigation are $0.88$ for **2(10)** and **2(12)** and $0.86$ for **2(14)**, meaning that their molecular array must be closer to that of a normal calamitic liquid crystal (i.e. the $HL_2(n)$ compounds) than that suggested for the $\{Pd[L_2(n)](\mu\text{-Cl})\}_2$ dimers.

## 4. Conclusion

In conclusion, the preparation of new calamitic chiral low melting mononuclear palladium mesogens has been achieved. On the whole, the results obtained confirm that the molecular geometry featured by these 'P-shaped' $LPd(acac)$ compounds confers better liquid crystalline properties upon them than does the 'H-shaped' arrangement of the $L_2Pd$ or $L_2Pd_2$ complexes, and suggests that, with reference to the $HL$ cyclopalladated derivatives, if the ligands required to complete the palladium coordination sphere are small, the mesomorphic behaviour improves.

## References

[1] GHEDINI, M., MORRONE, S., FRANCESCANGELI, O., and BARTOLINO, R., *Molec. Crystals liq. Crystals* (in the press).
[2] GHEDINI, M., PUCCI, D., CESAROTTI, E., FRANCESCANGELI, O., and BARTOLINO, R., 1993, *Liq. Crystals*, **15**, 331.
[3] GHEDINI, M., PUCCI, D., CESAROTTI, E., ANTOGNIAZZA, P., FRANCESCANGELI, O., and BARTOLINO, R., 1993, *Chem. Mater.*, **5**, 883.
[4] ESPINET, P., EXTEBARRIA, J., MARCOS, M., PEREZ, J., REMON, A., and SERRANO, J. L., 1989, *Angew. Chem., Int. Ed. Engl.*, **28**, 1065.
[5] GHEDINI, M., and PUCCI, D., 1990, *J. organomet. Chem.*, **395**, 105.
[6] BAENA, M. J., ESPINET, P., ROS, M. B., and SERRANO, J. L., 1991, *Angew. Chem., Int. Ed. Engl.*, **30**, 711.
[7] GHEDINI, M., PUCCI, D., ARMENTANO, S., BARTOLINO, R., VERSACE, C., CIPPARRONE, G., and SCARRAMUZZA, N., 1992, N. Italian Patent VE 92A000 003, 16 January.
[8] ESPINET, P., ESTERUELAS, M. A., ORO, L. A., SERRANO, J. L., and SOLA, E., 1992, *Coord. Chem. Rev.*, **117**, 215.
[9] TAYLOR, E. C., HAWKS, G. H., and McKILLOP, A., 1968, *J. Am. chem. Soc.*, **90**, 2421.
[10] ONUE, H., and MORITANI, I., 1972, *J. organomet. Chem.*, **43**, 431.
[11] COCKBURN, B. N., HOWE, D. V., JOHNSON, B. F. G., and LEWIS, J., 1973, *J. chem. Soc. Dalton Trans.*, p. 404.