Published in Journal of Materials Chemistry 12 : 2653 - 2658, 2002
which should be used for any reference to this work

Hexacatenar liquid-crystalline complexes of palladium(II) and platinum(II) based on trialkoxystilbazole esters

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Received 22nd April 2002, Accepted 13th June 2002
First published as an Advance Article on the web 30th July 2002

The synthesis and characterisation of 4-(3′,4′,5′-trialkoxybenzoyloxy)pyridines (**1a–e**), and of their corresponding palladium(II), (**2a–e**), and platinum(II), (**3a–e**), complexes are described. The pyridine-based ligands are not mesomorphic, but upon complexation to $PdCl_2$ or $PtCl_2$, new hexacatenar mesogens are formed which show exclusively the hexagonal columnar mesophase. The mesomorphic behaviour of the complexes was characterised by polarised optical microscopy, differential scanning calorimetry and X-ray diffraction. The metal seems to influence the crystal phase and mesophase stability as well as the mesomorphic temperature range.

Introduction

The past two decades have witnessed a steadily growing interest in the synthesis of metal-containing liquid crystals[1] (metallomesogens) in the expectation of combining some specific properties of transition metals (*e.g.* optical, magnetic and electronic) with the exceptional properties of anisotropic fluids. In addition, particular attention has been directed towards a better understanding of the relationships between the shape and nature of a complex and the structure of the mesophase. The complexation of a metallic centre to an organic species which is mesomorphic or simply mesogenic, can indeed have dramatic effects on the thermal behaviour of the latter, such as mesophase formation, modification or even suppression. These effects result from the influence of a variety of factors including change in polarisability, change in molecular anisotropy, modification of the polar/dipolar characteristics and so on.

Calamitic, square-planar metal complexes of the type *trans*-$[MX_2L_2]$, where L is a mesogenic, monodentate ligand and X is a halide, a carboxylate or a tertiary phosphine group, are appropriate systems for such studies, since structural variations are relatively straightforward to carry out. For instance, *trans*-$[PdX_2L_2]$ and *trans*-$[PtX_2L_2]$ complexes with anisotropic nitrile,[2] stilbazole,[3] alkynyl,[4] isonitrile[5] and carbene[6] groups have been studied intensively. On account of their linear, calamitic shape, it is therefore not surprising that they show nematic and/or smectic phases. An interesting structural variation related to this study consisted in the coordination of ligands possessing several terminal chains. The resulting complexes, which are polycatenar mesogens,[7] contain typically between four and six alkoxy chains, in these cases disposed symmetrically with an equal number at each end of the complex. According to the number and the length of the peripheral alkoxy chains, a remarkably diverse mesomorphism can be observed for polycatenar mesogens, including nematic, smectic, columnar and cubic phases, with sometimes several of them occurring in a single compound as a function of temperature.[8,9] Polycatenar mesogens therefore form an interesting class of materials to study as they bridge the gap between the mesomorphism of purely calamitic and purely discotic mesogens. Such studies are still rare with these types of complexes and only a few polycatenar metallomesogens of Pt(II) and Pd(II) have been reported, notably with polyalkoxy-4-stilbazole (**4**),[10] 3,4,5-trialkoxystyrylstilbazole (**5**),[11] 3,4,5-trialkoxybenzonitrile (**6**),[12] 3,4,5-trialkoxyphenylisonitrile (**7**)[13] ligands (Fig. 1). Note that there are also novel examples of polycatenar metallomesogens with different metal atoms such as iron,[14] chromium,[15] copper,[16] mercury,[17] silver[9,18] and gold,[18] oxovanadyl[19] or built from zinc porphyrins,[20] and palladium crown-ethers.[21]

Following on from our earlier studies of polycatenar metal complexes based on polyalkoxystilbazole ligands, we report in this paper the synthesis and mesomorphism of two new series of hexacatenar complexes of palladium(II) and platinum(II) based on 4-(3′,4′,5′-trialkoxybenzoyloxy)pyridine ligands.

Results and discussion

Synthesis

The synthetic pathway used to prepare the 4-(3′,4′,5′-trialkoxybenzoyloxy)pyridine ligands (**1a–e**, L) is shown in Scheme 1. The first step consisted of the etherification of methyl 3,4,5-trihydroxybenzoate with the appropriate 1-bromoalkane, with the resulting methyl trialkoxybenzoate being hydrolysed to the corresponding benzoic acid using potassium hydroxide in ethanol. The target ligands were then obtained by the esterification of the 3,4,5-trialkoxybenzoic acid with 4-hydroxypyridine using 4-pyrrolidinopyridine (4-PPy) and dicyclohexylcarbodiimide (DCC) in chloroform. The complexes $[PdCl_2L_2]$ (**2a–e**) and $[PtCl_2L_2]$ (**3a–e**) were then prepared by one of two methods (Scheme 1). The palladium complexes were prepared by reaction of the ligand with $[PdCl_2(PhCN)_2]$ in acetone at room temperature (Scheme 1, route a). However, the platinum complexes were prepared using a melt synthesis[22] in which one equivalent of platinum dichloride was added to three equivalents of the molten ligand and stirred for half an hour at 140 °C (Scheme 1, route b). Both reactions proceeded in moderate-to-good yields. The complexation of the pyridine

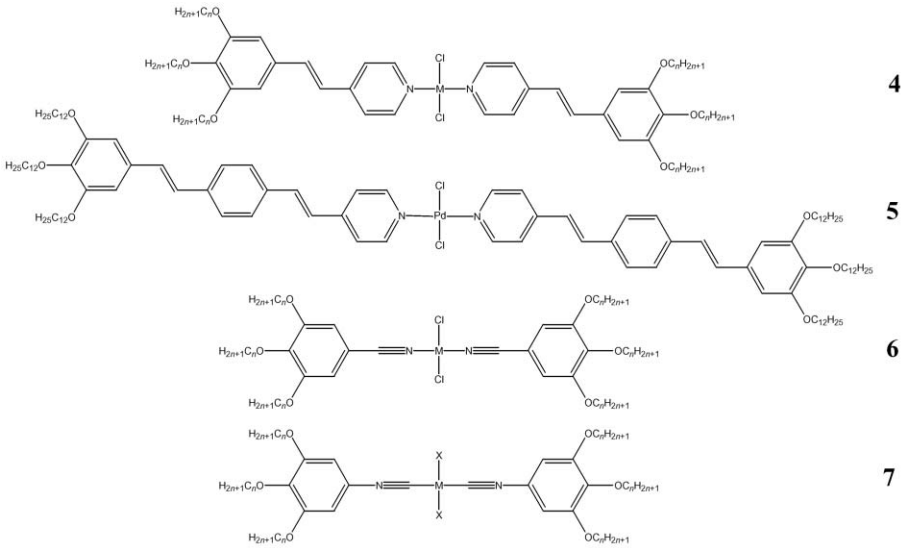
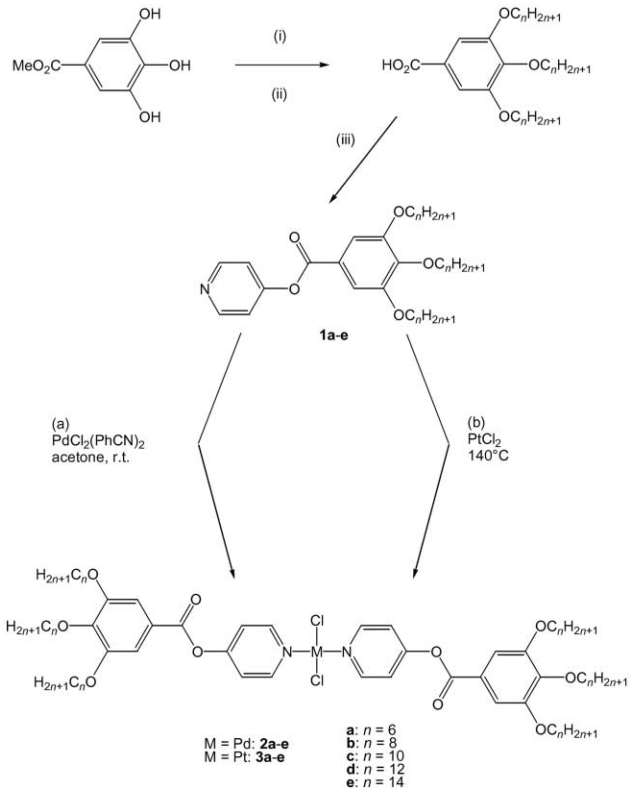


Fig. 1 Structure of other hexacatenar metallomesogens (**4–7**).



Scheme 1 Synthesis of 4-(3′,4′,5′-tri(alkoxy)benzoyloxy)pyridine ligands (**1a–e**)—(i) $C_nH_{2n+1}Br$, $KHCO_3$; (ii) KOH/EtOH; (iii) 4-hydroxypyridine, DCC, 4-PPY—and of the palladium (**2a–e**) and platinum (**3a–e**) complexes.

based-ligands was confirmed by ^1H NMR spectroscopy and elemental analysis. The ^1H NMR spectra of both the free ligands and the metal complexes were very similar, but a significant increase of the chemical shifts of the pyridine protons *ortho* to the ring nitrogen was observed upon complexation (δ 8.39 to 8.88 (Pd) or δ 8.96 (Pt)) as expected due to the attachment of the ring to the electron deficient metal fragments.

Thermal behaviour of the complexes

Although the pyridine based-ligands were not mesomorphic, their complexation to $PdCl_2$ and $PtCl_2$ led to new, hexacatenar mesogens, most of which showed enantiotropic mesophases at accessible temperatures. This is another example of mesophase induction on coordination to a metal.[1] The transition temperatures were determined by both polarised optical microscopy and differential scanning calorimetry, while confirmation of the identity of the mesophase was made on the basis of the optical texture and by small-angle X-ray diffraction (XRD). The mesomorphic behaviour of the two series of compounds is illustrated graphically in Fig. 2. The transition temperatures and associated transition enthalpies for the whole series of complexes, and the indexation of the X-ray reflections and the relevant mesophase parameters, are gathered in Tables 1 and 2, respectively.

Complex **2a** did not show any liquid-crystalline properties and melted directly into the isotropic liquid at 120 °C after undergoing a crystal–crystal transition at 111.5 °C. However, on the second heating, the original higher-temperature crystalline phase was not observed, and **2a** melted directly into the isotropic liquid at 110.5 °C. From the DSC experiment, it seemed clear that the crystal phase which melted at 120 °C on first heating is the thermodynamic stable state at these temperatures as this phase did not immediately form on cooling and did not have the time to *reform* from the crystal phase which was obtained on cooling from the melt. Thus, it seems that different crystal modifications are obtained from melt and solution crystallisation. On heating, **2b** gave rise to two crystalline phases prior to a birefringent fluid phase at 93 °C. This phase existed over a narrow temperature range

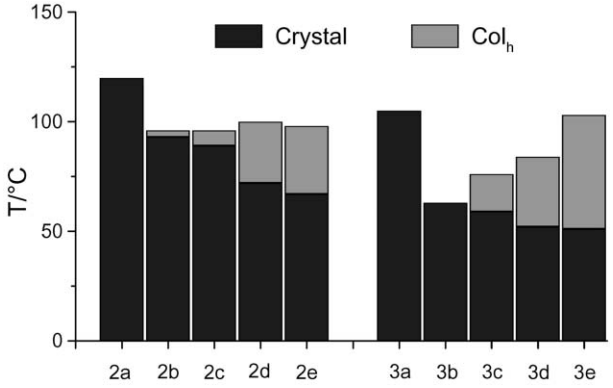


Fig. 2 Phase diagram of the *trans*-dichlorobis(3′,4′,5′-tri(alkoxy)-benzoyloxy-4-pyridine)palladium(II) complexes (**2a–e**) and of the *trans*-dichlorobis(3′,4′,5′-trialkoxybenzoyloxy-4-pyridine)platinum(II) complexes (**3a–e**).

Table 1 Transition temperatures and corresponding enthalpy changes of the *trans*-dichlorobis(3′,4′,5′-trialkoxybenzoyloxy-4-pyridine)palladium complexes (**2a–e**), and of the *trans*-dichlorobis(3′,4′,5′-trialkoxybenzoyloxy-4-pyridine)platinum (**3a–e**), complexes, recorded at 5 °C min^{-1}. (Crys, Crys′: crystalline phases; Col_h: hexagonal columnar phase; IL: isotropic liquid)

	1st Heating	T/°C	ΔH/kJ mol^{-1}	2nd Heating	T/°C	ΔH/kJ mol^{-1}
2a	Crys–Crys′	111.5	25.5	—	—	—
	Crys′–IL	120	12.3	Crys–IL	110.5	26.2
2b	Crys–Crys′	47	105.1	—	—	—
	Crys′–Col_h	93	17.5	Crys′–Col_h	92.5	15.1
	Col_h–IL[a]	96	—	Col_h–IL[a]	96	—
2c	Crys–Crys′	41	122.3	—	—	—
	Crys′–Col_h	89	5.9	Crys′–Col_h	88	5.4
	Col_h–IL	96	4.7	Col_h–IL	96	4.4
2d	Crys–Crys′	32	53.5	—	—	—
	Crys′–Col_h	72	6.0	Crys′–Col_h	75	10.4
	Col_h–IL	100	4.7	Col_h–IL	100	4.8
2e	Crys–Crys′	43	140.7	—	—	—
	Crys′–Col_h	67	4.5	Crys′–Col_h	66	8.0
	Col_h–IL	98	2.6	Col_h–IL	97	4.5
3a	Crys–IL	105	51.7	—	—	—
3b	Crys–Crys′	46	120.1	Crys–Crys′	46	120.7
	Crys′–IL	63	24.2	Crys′–IL	57	12.3
3c	Crys–Crys′	33	10.2	—	—	—
	Crys′–Col_h	59	9.8	Crys′–Col_h	48	5.4
	Col_h–IL	76	3.6	Col_h–IL	76.5	3.6
3d	Crys–Crys′	43	110.1	—	—	—
	Crys′–Col_h	52	6.3	Crys′–Col_h	56	10.2
	Col_h–IL	84	4.0	Col_h–IL	84	4.0
3e	Crys–Crys′	39	106.1	—	—	—
	Crys′–Col_h	51	29.7	Crys′–Col_h[a]	53	—
	Col_h–IL	103	—	Col_h–IL	103	—

[a]Determined by POM.

Table 2 Indexation and structural parameters of the Col_h phase of **2c–e** and **3c–e**

	T/°C	d_{10}/Å	d_{11}/Å	d_{20}/Å	d_{21}/Å	h_1/Å	h_2/Å	a[a]/Å	s[a]/$Å^2$	V_{mol}	N_{mol}
2c	80	31.8	18.2	15.7	12.1	8.5	4.5	36.6	1160	2470	4.0
2d	80	33.6	19.4	16.9	12.7	8.8	4.6	38.85	1307	2790	4.1
2e	80	35.4	20.4	17.7	—	8.8	4.5	40.85	1445	3070	4.1
3c	60	31.7	18.3	16.0	12.0	8.9	4.6	36.7	1167	2620	4.0
3d	80	33.2	19.1	16.6	12.5	9.0	4.6	38.3	1270	2940	3.9
3e	80	34.7	20.0	17.3	—	9.1	4.6	40.0	1386	3220	3.9

[a]The intercolumnar distance, a, and the columnar cross-sectional area, s, were calculated according to: $a = 2/\sqrt{3}<d_{10}>$ and $s = 2/\sqrt{3}<d_{10}>^2$, where $<d_{10}> = ¼<d_{10} + \sqrt{3}d_{11} + 2d_{20} + \sqrt{7}d_{21}>$.

and cleared to the isotropic liquid at 96 °C; the mesophase reappeared at 90 °C on cooling. On subsequent heating, the first crystalline phase did not reappear, but the same birefringent phase was once again observed in the same temperature range. Because of this narrow temperature range, it was not possible to obtain an X-ray diffraction pattern of the mesophase, but the optical texture was consistent with the formation a columnar hexagonal phase. Complexes **2c**, **2d** and **2e** all behaved similarly and were mesomorphic, displaying a single mesophase after undergoing one crystal–crystal transformation, the lower-temperature crystalline phase being absent on subsequent cooling and heating cycles. On slow cooling of the samples from the isotropic liquid, optical microscopy showed the growth of developable and cylindrical monodomains, characteristic of a columnar phase and consistent with assignment as a hexagonal phase. In this series, the melting point decreased with increasing chain length, rather steeply between **2a** and **2b**, and then stepwise for the higher homologues, whereby the clearing temperatures remained almost unchanged for **2b–e**. Consequently, the mesomorphic range was firstly enlarged, and then reached a maximum.

XRD experiments were carried out at different temperatures in the mesophase (Table 2, Fig. 3). The X-ray patterns consisted of three, and sometimes four, sharp and intense reflections in the small angle region and of two diffuse scattering halos in the wide angle region at 8.5–8.8 Å (h) and at *ca.* 4.5 Å. The outer diffuse halo corresponds to the liquid-like order of the molten hydrocarbon chains, while the inner one has been assigned to the stacking periodicity along the columnar axis. The ratio of the intense reflections correlates well with the theoretical 1, $\sqrt{3}$, $\sqrt{4}$ and $\sqrt{7}$ reciprocal spacing

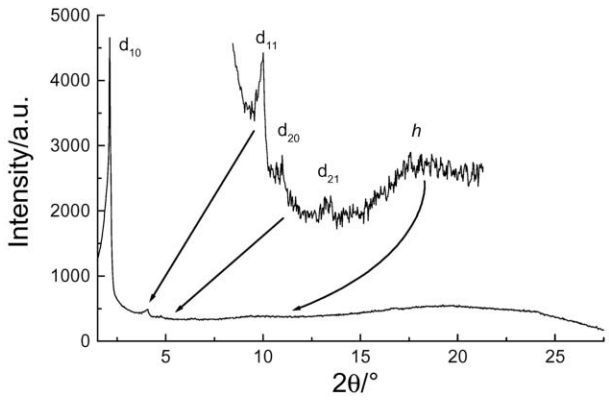


Fig. 3 Representative X-ray pattern of a Col_h phase (**2d**, at 80 °C).

ratio, corresponding to the indexation (hk) = (10), (11), (20) and (21), characteristic of a two-dimensional hexagonal packing of columns.

The first two homologues of the platinum series, **3a** and **3b**, did not show any liquid-crystalline properties, and before clearing, **3b** showed a crystal-to-crystal transformation. The thermal behaviour of **3b** was almost completely reproduced, except that it clears into the isotropic liquid at a lower temperature than that in the first heating. However, **3c**, **3d** and **3e** melted into a mesophase, which was assigned by optical microscopy as a Col_h phase on the basis of the growth of the well-recognisable, developable monodomains and of the presence of large homeotropic areas. For these three compounds, the crystal–crystal phase transition disappeared on cooling and did not reappear. Note that the mesophase range of **3c** has been extended slightly on the second heating, with respect to the first one, in that the new crystalline phase melts into the mesophase 10 °C lower while the clearing point remains unchanged. The melting point decreased with increasing chain length, very steeply between the two first homologues, but then smoothly afterwards, whereas the clearing temperature kept increasing from **3c** to **3e**, consequently yielding an enlarged mesomorphic domain.

The X-ray patterns of the mesophase consisted of three, and sometimes four, sharp and intense reflections in the small-angle region with reciprocal spacings in the ratio 1, $\sqrt{3}$, $\sqrt{4}$ and $\sqrt{7}$ corresponding to (hk) indexation, (10), (11), (20), and (21), confirming the identity of hexagonal columnar phase. As was the case for **2**, the same two diffuse scattering halos in the wide angle region at 9.0 Å (h) and at *ca.* 4.6 Å were also observed, and the same explanations are given.

Discussion

As expected with this structural type, these materials show columnar phases, providing that each peripheral chain contains at least eight carbon atoms for the palladium complexes and ten for their platinum congeners. Both metal complexes have a square-planar geometry with the two mesogenic ligands in the *trans*-configuration. Such disposition leads to an elongated rod-molecule consistent with the general motif for polycatenar mesogens. As an explanation for this behaviour, one has to consider an important factor governing the self-assembly of the molecules, and the resulting spatial organisation of the columns so formed, namely the volume ratio between that of the rigid core and that of the flexible chains, and the related mismatch between the cross-sectional area of the rigid core and that required by the chains at the aromatic/aliphatic interface. Where two chains are attached to each end of a polycatenar mesogen, this mismatch leads to the formation of a tilted (SmC) mesophase. As the chains get longer (and hence their volume increases), the increasing mismatch between core and chain volumes is accommodated initially by increased tilting of the cores and then by the creation of an undulating lamellar interface. This leads eventually to a break up of the lamellar structure and the formation of a columnar phase composed of aggregates of molecules.[10a,23] In the case of these hexacatenar complexes, the symmetric distribution of the terminal chains precludes the same tilting mechanism, but with the two additional chains, the chain/core volume mismatch is very much greater and columnar phases form directly.[24]

The 2D hexagonal symmetry of the columnar mesophases was characterised unambiguously by XRD for complexes **2c–e** and **3c–e**, with similar parameters for identical chain lengths. However, the mesophases exist at different temperatures and with different temperature ranges, suggesting some influence of the metal (Table 1). The overall decrease in the melting point is quite easily understood, due to the reduction in crystal packing efficiency caused by the poorer packing of longer chains in the solid state. However, no clear explanation can be given for the different behaviour of the clearing temperatures observed for each series.

It is also interesting to compare the thermal behaviour of these compounds with the structurally related palladium complexes of 3′,4′,5′-trialkoxy-4-stilbazoles.[10a] Palladium complexes of these ligands were synthesised (Fig. 1, **4**) from the nonyloxy homologue onwards and the complexes showed columnar mesophases, displaying both a low temperature Col_r mesophase and a higher temperature Col_h phase.[10a,25]

In these stilbazole complexes (**4**), the clearing point remained approximately constant with chain length, while the melting point varied, giving rise to mesomorphic ranges between 33 and 55 °C. Palladium complexes of the stilbazole esters in this paper (**2**) also showed a rather constant clearing point, but in addition showed a steadily decreasing melting point. Similar melting point behaviour was observed in the platinum congeners (**3**), but in addition there was a steady increase in the clearing point, so that for the tetradecyloxy homologue, the mesomorphic range in the new platinum complexes was 52 °C compared with 33 °C for the analogous palladium stilbazole complex and 31 °C for the corresponding Pd complex, **2e**. A significant difference between the new complexes and the stilbazole complexes is the presence of two appreciable dipole moments oriented towards the centre of the complex. In calamitic mesogens, such an arrangement of dipoles can destabilise lamellar phases[8] and so must hinder any side-by-side intermolecular interactions. The model postulated for the molecular arrangement in columnar phases of polycatenar mesogens requires some such interactions and so it is likely that the dipolar repulsion is readily overcome by the spatial requirements of the chains.

In order to get some idea of the molecular arrangement inside the column, one can estimate the number of complexes, N_{mol}, contained in each columnar repeat unit by dividing the volume of the elementary hexagonal cell, defined by s, the cross-section of the hexagonal columnar phase, and h, the stacking periodicity ($V_{cell} = hs$) by the molecular volume (V_{mol}), according to:

$$N_{mol} = hs/V_{mol}$$

A density of 1 g cm^{-3} was assumed, to calculate the molecular volume of complexes **2** and **3**. This approximation is reasonable and has been verified by means of the volume measurements of structurally related complexes,[10a,25] (Fig. 1, **4**). The calculation showed that, on average, about four molecules are needed to fill the volume of the elementary hexagonal cell, *i.e.* the columnar repeat unit, whatever the metal or the chain-length.

A model for the molecular organisation of these complexes in the Col_h phase can now be proposed. Let us first note that the crystalline phase shows a lamellar arrangement, as deduced from X-ray diffraction (sharp reflections in the ratio 1 : 2 : 3), with a spacing corresponding to a distance *ca.* 30% smaller than that calculated for the fully extended molecules. This suggests that the molecules could be arranged in an interdigitated or tilted manner in the initial crystalline phase (Fig. 4, **I**). The

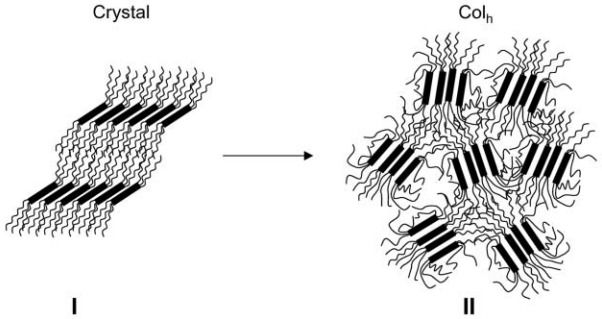


Fig. 4 Model for the formation of the columnar mesophase *via* a disordered lamellar structure.

transition into the second crystalline phase (see Table 1) is characterised by a slight increase in the interplanar spacings with a concomitant broadening of the small-angle reflections (the same behaviour was observed for almost all the samples), suggesting a partial deformation of the layers. It is also noticeable that this transition is accompanied by a large enthalpy change and that this change is very much greater than that found for the transition from this second crystalline phase to the columnar phase. As the temperature is raised, the increasing area occupied by the chains probably disturbs the layer planes; further thermal agitation then leads the chain conformation to become totally liquid-like and the molecular cores become fluid. A reorganisation then results which allows the structure to accommodate the conflicting volume requirements of both chains and cores, leading to the now familiar organisation within the columnar phase (Fig. 4, **II**). Given the relative magnitudes of the enthalpy changes for the Crys–Crys′ and the Crys′–Col_h transitions, it is, therefore, likely that the major reorganisation takes place at the former transition and that this phase will contain certain organisational features of the Col_h phase, even though X-ray diffraction shows that the hexagonal symmetry of the mesophase has not yet developed. In cases where the Crys–Crys′ enthalpy is lower than expected, the proximity of the initial transition to ambient temperature leads us to suppose that the samples are not totally crystalline.

In conclusion, the use of the hexacatenar 4-(3′,4′,5′-trialkoxybenzoyloxy)pyridine ligand permitted access to liquid-crystalline properties by complexation to palladium(II) and platinum(II). The complexes exhibit exclusively hexagonal columnar phases with quite low transition temperatures and on the basis of simple geometric arguments, it was possible to calculate the number of complexes needed to fill the repeat unit.

Experimental

All solvents were distilled prior to use according to standard procedures. The starting palladium complex, $[PdCl_2(PhCN)_2]$ was prepared as described previously.[23] ^{1}H NMR spectra were recorded on a Bruker ACL250 or AM400 spectrometer and referenced to external tetramethylsilane. Elemental analyses were performed by the ETH of Zurich microanalytical service. Infrared spectra were recorded on a Perkin-Elmer 1720-X spectrophotometer. Analyses by DSC were carried out using a Perkin-Elmer DSC7 instrument using various heating rates. Mesomorphism was studied by hot-stage polarising microscopy using a Zeiss Labpol microscope equipped with a Linkam TH600 hot-stage and PR600 temperature controller. The powder XRD patterns were obtained with the following experimental set-up; the crude powder was filled in Lindemann capillaries of 1 mm diameter. A linear monochromatic Cu-Kα_1 beam was obtained using a Guinier camera with a sealed-tube generator (900 W) equipped with an electric oven. The diffraction patterns were registered on an image plate; the cell parameter was calculated from the position of the reflection at the smallest Bragg angle, which was in all cases the most intense. Periodicities up to 90 Å can be measured, and the sample temperature is controlled within ± 0.3 °C. In each case, exposure times were varied from 1 to 24 h.

Synthesis of the 3,4,5-trialkoxybenzoic acids

All derivatives were prepared similarly and one representative preparation is given ($n = 8$). All other derivatives were obtained in yields ranging from 25–50%.

Methyl 3,4,5-trihydroxybenzoate (5 g, 27 mmol), potassium carbonate (22.5 g, 160 mmol) and 1-bromooctane (15.65 g, 82 mmol), were dissolved in butan-2-one (200 cm^3), and the reaction heated under reflux for 94 h. Water (100 cm^3) was added and the aqueous phase was extracted with dichloromethane (3 × 150 cm^3). The organic extracts were combined, dried over $MgSO_4$, filtered and evaporated to give a brown oil. A solution of potassium hydroxide (3.0 g, 45 mmol) in ethanol (95%, 150 cm^3) was added and the solution acidified with hydrochloric acid (concentrated, 20 cm^3). The resulting colourless precipitate was collected and crystallised twice from ethanol to give 3,4,5-tri(octyloxy)benzoic acid as a colourless solid. Yield 3.24 g (24%); IR (KBr, cm^{-1}): ν(CO) = 1688. ^{1}H NMR (250 MHz, $CDCl_3$, ppm) δ_H: 7.30 (2H, s, H^{Ar}), 4.01, 4.06 (6H, 2t, –OCH_2–), 1.79 (6H, qt, –OCH_2CH_2–), 1.50 (6H, m, –$OCH_2CH_2CH_2$–), 1.30 (24H, m, –$(CH_2)_4$–), 0.90 (9H, t, –CH_3).

Synthesis of the 4-(3′,4′,5′-trialkoxybenzoyloxy)pyridine (1a–e)

All the other derivatives were prepared similarly to $n = 8$, and obtained in yields ranging from 20–47%.

3,4,5-Trioctyloxybenzoic acid (2.30 g, 5.55 mmol), 4-hydroxypyridine (0.475 g, 5 mmol) and 4-pyrrolidinopyridine (4-PPY) (0.075 g, 0.51 mmol) in chloroform (30 cm^3) were stirred at 0 °C (15 min), and dicyclohexylcarbodiimide (1.032 g, 5 mmol) in $CHCl_3$ (10 cm^3) was then added. The mixture was stirred at room temperature for 17 h. After filtration and then evaporation of the solvent, the product was purified by chromatography using the solvent mixture petroleum ether (60–80)/ethyl acetate (7 : 3) as elution medium. Evaporation of the solvent gave a colourless oil. Cooling to −25 °C, a colourless solid was obtained. Yield 3.24 g (24%); IR (KBr, cm^{-1}) ν(CO) = 1739. ^{1}H NMR (250 MHz, $CDCl_3$, ppm) δ_H: 8.39 (2H, AA′XX′, $H^{o\text{-Py}}$, $J_{AA'XX'}$ 6.5 Hz), 7.39 (2H, s, H^{Ar}), 7.21 (2H, AA′XX′, $H^{m\text{-Py}}$, $J_{AA'XX'}$ 6.5 Hz), 4.08, 4.05 (6H, 2t, –OCH_2–), 1.84, 1.80 (6H, 2 qt, –OCH_2CH_2–), 1.49 (6H, m, –$OCH_2CH_2CH_2$–), 1.31 (24H, m, –$(CH_2)_4$–), 0.89 (9H, t, –CH_3).

Synthesis of the palladium complexes (2a–e)

All were prepared according to **2b**, chosen as the representative example. Yield and elemental analyses are collected in Table 3.

The complex $[PdCl_2(PhCN)_2]$ (0.27 g, 0.72 mmol) was dissolved in acetone (10 cm^3) and the relevant 4-(3′,4′,5′-trioctyloxybenzoloxy)pyridine (1.25 g, 2.15 mmol) in acetone (10 cm^3) was added dropwise to the stirring solution. The mixture was left stirring for 1 h until a precipitate formed. The compound was filtered off, washed with cold acetone and crystallised twice from hot acetone to give the pure product in 73% (0.705 g) yield. IR (KBr, cm^{-1}): ν(CO) = 1740. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ_H: 8.88 (4H, AA′XX′, $H^{o\text{-Py}}$, $J_{AA'XX'}$ 6.5 Hz), 7.35 (4H, s, H^{Ar}), 7.32 (4H, AA′XX′, $H^{m\text{-Py}}$, $J_{AA'XX'}$ 6.5 Hz), 4.08, 4.05 (6H, 2t, –OCH_2–), 1.86, 1.76 (12H, 2qt,

Table 3 Analytical data for the palladium and platinum complexes

		Found (calculated) (%)		
	Yield (%)	C	H	N
2a	78	61.10 (61.24)	7.80 (7.71)	2.37 (2.38)
2b	73	64.09 (64.09)	8.37 (8.54)	2.08 (2.08)
2c	67	66.40 (66.67)	9.46 (9.19)	1.83 (1.85)
2d	48	68.40 (68.57)	9.83 (9.71)	1.75 (1.67)
2e	40	70.06 (70.12)	9.97 (10.13)	1.61 (1.51)
3a	61	56.99 (56.95)	7.30 (7.17)	2.28 (2.21)
3b	53	60.28 (60.32)	8.15 (8.01)	2.02 (1.95)
3c	43	63.27 (62.98)	8.72 (8.68)	1.73 (1.75)
3d	69	65.28 (65.13)	9.00 (9.22)	1.55 (1.58)
3e	54	67.16 (66.91)	9.48 (9.67)	1.49 (1.45)

–OCH_2CH_2–), 1.49 (12H, m, –$OCH_2CH_2CH_2$–), 1.30 (48H, m, –$(CH_2)_4$–), 0.89 (18H, t, –CH_3).

Synthesis of the platinum complexes (3a–e)

All were prepared according to **3b** chosen as the representative example. Yield and elemental analyses are collected in Table 3.

Platinum dichloride (0.075 g, 0.28 mmol) was added in small portions to the molten 4-(3′,4′,5′-trioctyloxybenzoyloxy)pyridine (0.565 g, 0.85 mmol), and the mixture was stirred at 140 °C for 90 min. A yellow–orange oil was obtained. It was dissolved in $CHCl_3$ (10 cm^3), the solution was filtered through a pad of Celite (to remove the unreacted $PtCl_2$), which was washed with chloroform (2 × 5 cm^3). After evaporation of the chloroform, the yellow oil obtained was dissolved in acetone. Upon cooling to −25 °C a colourless precipitate was formed. Washed with cold acetone, the complex was recovered by crystallisation from hot acetone in 43% (0.187 g) yield. IR (KBr, cm^{-1}): ν(CO) = 1741. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ_H: 8.96 (4H, AA′XX′, $H^{o\text{-Py}}$, $J_{AA'XX'}$ 6.5 Hz), 7.35 (4H, s, H^{Ar}), 7.30 (4H, AA′XX′, $H^{m\text{-Py}}$, $J_{AA'XX'}$ 6.5 Hz), 4.08, 4.04 (12H, 2t, –OCH_2–), 1.85, 1.75 (12H, 2qt, –OCH_2CH_2–), 1.49 (12H, m, –$OCH_2CH_2CH_2$–), 1.32 (48H, m, –$(CH_2)_4$–), 0.89 (18H, t, –CH_3).

Acknowledgements

We thank the Universities of Neuchâtel and Exeter, the Fonds National Suisse de la Recherche Scientifique and the European Union SOCRATES programme (L. P. and L. G. C.) for financial support of this work.

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