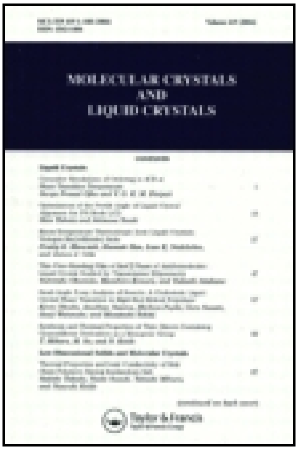

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Amphotropic Properties of Multi-Palladium and -Platinum Liquid Crystals [1]

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Amphotropic Properties of Multi-Palladium and -Platinum Liquid Crystals [1]

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Tetrametallomesogens containing palladium (**2**,**3a–c**) or platinum (**4**,**5a–c**) macroheterocyclic central cores show wide ranging liquid crystalline properties, both thermotropic and lyotropic in apolar organic solvents. Here, we present an overview of recent work from our laboratory concerning these novel metallomesogens and related bis-metal analogues **6** and **7**. We also propose new nomenclature to satisfy the growing range of liquid crystalline mesophases exhibited by these materials.

Keywords: Arylimines; heterocycles; lyo- and thermo-mesomorphism; mesophases; metal (Pd and Pt) organyes; ortho-metallations

INTRODUCTION

Metal containing liquid crystals (metallomesogens) are growing in importance and have been investigated by a growing number of groups in recent years, for an overview see seven reviews [2] which have appeared since 1991. The attraction of metallomesogens rests on the promise of new materials combining the properties of metal complexes along side those of a liquid crystal mesophase.

Cyclometallated complexes containing platinum group metals [3] have considerable commercial and academic interest. Such functionality has been

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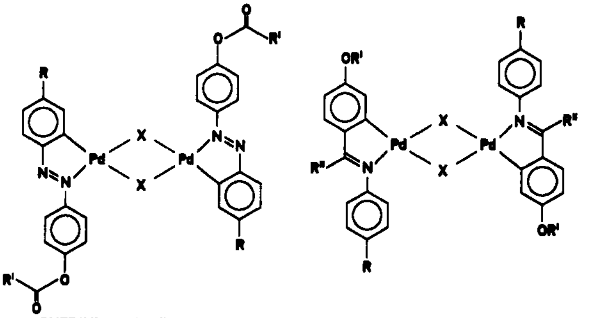
incorporated into metallomesogens primarily as cyclopalladated azobenzene [4], diarylazine [5], phenylpyrimidine [6] and most importantly in the context of our work since 1990, arylimine [7] complexes. These materials [4–7] are typically *bis*-metallic H-shaped complexes consisting of a *twinned* rod-like structure, or *mono*-metallic complexes where the bridging ligands are replaced by acetylacetonate to give P-shaped materials and display mesophases typical of calamitic liquid crystals (*i.e.* smectic and nematic phases) consistent with their rod-like structure.

In contrast, we have prepared *bis*-palladium arylimine complexes [8] and more recently the first examples of cycloplatinated metallomesogens [9] which, though containing the same central core as those of Espinet and co-workers [5, 7] display mesophases characteristic of flat, disc–like materials (in both thermotropic and lyotropic systems). This is clearly due to the incorporation of additional lateral substituents into the ligands (shown as highlighted ether functionalities in our example in Fig. 1) which perturbs the overall geometry of the complex leading to a generalised disc–like rather than rod-like shape. These compounds are interesting since they are an example of the same central metal coordination core yielding both rod-and disc-like shapes depending on peripheral substitution plattern. It has been suggested[2(ii)] that our flat metal organyls are close to a calamitic/discotic crossover point and that it might be anticipated that they will show mesogenic behaviour with some characteristics of each phase type, in particular the possibility of biaxiality and associated fast switching effects.

We first looked at the effect of peripheral substitution on the mesomorphic properties of organic materials in general over ten years ago [10] and since our first report of related tetrapalladium *bis*–diiamine complexes (see Scheme 1) some seven years ago [8], we have become increasingly interested in the influence that the peripheral substitution, bridging ligand and metal atom type have on the mesomorphism of these compounds.

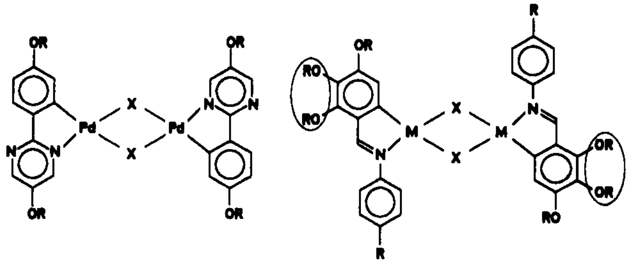
Here, we provide a perspective on recent work in our laboratory centred on the investigation of metallomacrocylic tetrapalladium [8, 11–13] and –platinum [9, 14] sheet-like materials (Scheme 1) with different halogen metal-metal bridging ligands and with different lengths in their peripheral aliphatic chains. These materials display wide ranging liquid crystalline mesomorphism, both thermotropic and lyotropic [12, 14–16] in apolar organic solvents including two lyotropic nematic columnar phases side by side and also interesting *induced* mesophase formation [16–18] in the presence of small organic electron acceptors (*i.e.* TNF or TAPA [19]).

The tetrametal compounds may be regarded as consisting of two multicatenar parts derived from the two bisimine ligands, linked via a metal-



GHEDINI et al., ITALY, 1982,
X = Cl, Br, I

ESPINET et al.,SPAIN, 1987
X = Cl, Br, SCN

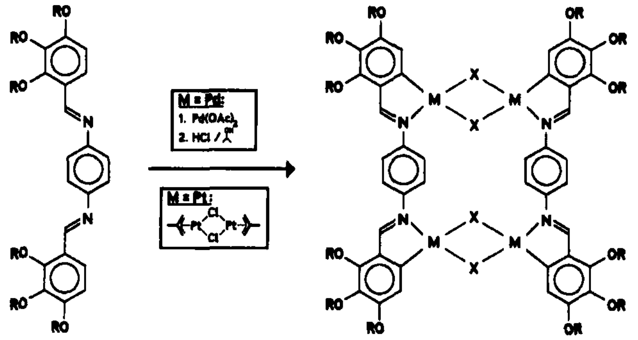


GHEDINI et al., ITALY, 1991,
X = Cl, Br, I

Our laboratory,
M = Pd (1992) or Pt (1994),
X = Cl, Br, I, SCN, N_3

FIGURE 1 The basic structural motifs of cyclometallated dinuclear mesogens (R,R′ = long alkyl chains, R″ = H,CH_3); azobenzene [4] (*top left*), phenylpyrimidine [6] (*bottom left*), arylimine [7] (*top right*; related diarylazine$^{5(ii)}$ optically active complexes were the first examples of ferroelectric metallomesogens) and laterally substituted arylimine complexes [8, 9] (*bottom right*) from our laboratory. The addition of lateral substituents (*ringed*) in our examples is responsible for the change in characteristic mesomorphic behaviour from calamitic (mostly smectic) observed for the other examples to nematic discotic (N_D) or columnar.

lo-macrocyclic core in which each ligand is bis-metallated. The structure of the complexes has been determined by combinations of osmometry, mass spectroscopy and by single crystal X-ray diffraction. The thermotropic mesomorphism of complexes has been investigated using a combination of optical microscopy, differential scanning calorimetry (DSC) and small angle X-ray scattering. From the single crystal X-ray diffraction studies [13] of the palladium dodeca*hexyloxy*, *iodo*-bridged compound **2c** and the dodeca*methoxy*, *bromo* homologue [20], it is clear that the planarity and overall geometry of the metallomacrocyclic core of this family of compounds is preserved independently of the nature of the halogen bridges and so presents a flat metallo-aromatic core with twelve alkoxy substituents arranged around the periphery.



1

R = C_6H_{13} or $C_{12}H_{25}$

	M	R	X
2	Pd	C_6H_{13}	a: Cl, b: Br, c: I
3	Pd	$C_{12}H_{25}$	a: Cl, b: Br, c: I
4	Pt	C_6H_{13}	a: Cl, b: Br, c: I
5	Pt	$C_{12}H_{25}$	a: Cl, b: Br, c: I

SCHEME 1 Synthesis of the tetrametallomesogen series **2–5**. The cyclometallation reactions [8, 13, 14] yield the related products without notable polymer formation. Therefore a template effect of the metal atoms is assumed [14]·

SYNTHESIS

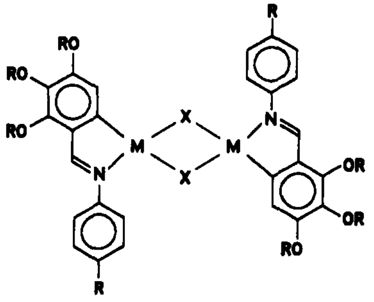
The ligands **1** for the series **2–5** are synthesised from pyrogallol. Etherification with dodecylbromide or hexylbromide, respectively, gives the related triethers which after a subsequent Vilsmeyer formylation yield the 2,3,4-tri(alkyloxy) derivatives of benzaldehyde. The complete ligands are then obtained by condensation of these aldehydes with 1,4-benzenediamine to give the corresponding Schiff bases **1** with R = hexyl or dodecyl [8, 21].

The cyclometallated compounds with chloro-bridges **2–5a** are then obtained by application of ortho-palladation or ortho-platination reactions to the imines **1** – see scheme 1 [8, 13, 14].

Ortho-*palladation* to yield **2a** and **3a** is carried out by using palladium *acetate* as a percursor. Thus reaction of palladium acetate with the imine compounds **1** in concentrated acetic acid solution leads to the aceto-bridged palladium organyls [22] first, which are then converted into the chloro-bridged compounds by subsequent reaction with diluted isopropanolic hydrochloric acid. In contrast, the ortho-*platination* is achieved by using a dichloro-platinum reagent di-μ-chloro-bis-(η^3-2-methylallylplatinum) [23] so that the desired chloro-bridged platinum complexes are obtained directly [14]. Compounds with other halogenobridging groups

2–5b,c are prepared from the parent chloro-bridged compounds by exchange of the halogen atoms. This exchange is done by simply stirring the complexes with either potassium bromide or lithium iodide in dichloromethane/acetone at room temperature for ca. 5 days [8, 11, 14]. The structures of the resulting products have been proved by IR, NMR and mass spectroscopy [8, 11, 14], osmometric molecular weight determinations [8] and finally for the tetrapalladium mesogens even by single crystal X-ray studies [13]. It is interesting to note that these cyclometallation reactions occur with high yields for the Pd-series (60–90%) [8, 11] but with somewhat poorer yields for the Pt-series (30%) [9, 14]. In all cases oligomerisation was not observed. Therefore, for both cyclometallations (involving palladium or platinum) a self-assembling process was assumed [14], using these metal atoms as shape-templates and thus controlling the clean formation of the tetrametal macroheterocycles of molecular structure **2–5** (Scheme 1) in a novel type of metal induced "dimerisation" reaction.

The dinuclear metallomesogens **6** and **7** (Fig. 2) are prepared by the same reaction sequence as depicted above: first the ligands were made by the usual condensation reactions, here between 4-alkylaniline and 2,3,4-tri(alkyloxy)benzaldehyde, then the cyclometallation reactions were carried out subsequently followed by the exchange reactions for the different bridging groups [8, 9]. The anti-parallel orientation of the ligands in series **6** and **7** were shown by NMR [8, 9] and single crystal X-ray scattering [9, 24]. The yields are comparable to those of the tetranuclear series **2–5**. Again cyclometallation with platinum gives much poorer yields than with palladium.



	M	R	X
6	Pd	C_6H_{13}	a: Cl, b: Br, c: I
7	Pt	C_6H_{13}	a: Cl

FIGURE 2 The mesomorphic bis-palladium and - platinum complexes **6** and **7** [8, 9].

THERMOTROPIC PHASE BEHAVIOUR

The *bis*-metallated complexes **6a–c** [8] and **7a** [9] show relatively simple, restricted mesomorphism. On heating, the compounds melt to the isotropic liquid between about 79–98°C and on cooling display monotropic nematic mesophases with Schlieren texture at 27–44°C. Following miscibility studies, it was confirmed that the nematic phase observed, was in all cases a nematic discotic N_D phase. These compounds were the first examples of cyclometallated metallomesogens forming this type of phase in contrast to calamitic phases. This indicates that control of the peripheral substitution pattern provides a good mechanism for strong influence on the phase behaviour. The phase formation is significantly different to that of the related compounds prepared by other groups [4–7] as a direct result of the lateral substituents incorporated in the aromatic 2 and 3-positions of their ligands.

Whereas these compounds have a disc-like structure and related mesophase behaviour as a function of the ligand lateral-substitution pattern, the tetrametallated compounds **2–5** display a slightly different control mechanism. In the case of these compounds, the disc-like central core of the complexes is prepared by using related ligands which can be cyclometallated *twice* on each ligand to yield the large flat molecular topology by their metal and halogen bridged "dimerisation".

Discussion of the thermotropic liquid crystal properties of the tetracyclometallated organyls is restricted here to two representative series of palladium and platinum compounds with halogen-brigdes (X = Cl,Br,I) and either twelve hexyloxy (**2a–c**,**4a–c**) or dodecyloxy chains (**3a–c**,**5a–c**) around the periphery of the molecules. All the complexes described, with the exception of the chloro-bridged hexyloxy-palladium compound (**2a**), display thermotropic mesomorphism, see Table I.

For the shorter chain (hexyloxy) compounds (**2a–c**,**4a–c**), in all examples except **2a**, a single columnar mesophase is obtained from around 100°C and persists to high clearing points in excess of 300°C. The palladium chloro-bridged **2a** compound unusually shows no mesomorphism, melting at 332°C. In all cases, clearing to the isotropic liquid is associated with strong decomposition.

With the longer chain compounds (**3a–c**,**5a–c**), again a single columnar mesophase is obtained although in these compounds, with somewhat lower transition temperatures around 60–70°C for the crystal–mesophase transition. Clearing temperatures are also lowered slightly in comparison to the hexyloxy-analogues, being between 265–300°C. Only a single mesophase is observed over this temperature range, though the bromo-bridged platinum

TABLE I Thermotropic phase transition temperatures (°C) for the tetrapalladium [8, 13] (**2a–c**,**3a–c**) and -platinum [14] (**4a–c**,**5a–c**) liquid crystals; Cr: crystalline, Col_{ob}: columnar oblique mesophase, Iso: isotropic liquid and dec.: decomposition

	M	*R*	*X*	*Cr*		*Col_{ob}*		*Iso*	
2a	Pd	C_6H_{13}	Cl	●	332	–		●	dec.
b			Br	●	103	●	306	●	dec.
c			I	●	123	●	306	●	dec.
3a	Pd	$C_{12}H_{25}$	Cl	●	71	●	301	●	dec.
b			Br	●	69	●	279	●	dec.
c			I	●	62	●	265	●	dec.
4a	Pt	C_6H_{13}	Cl	●	100	●	357	●	dec.
b			Br	●	111	●	341	●	dec.
c			I	●	107	●	328	●	dec.
5a	Pt	$C_{12}H_{25}$	Cl	●	70	●	280	●	dec.
b			Br	●	68	●	292	●	dec.
c			I	●	55	●	297	●	dec.

compound **5b** does show some additional unidentifed polymorphism by DSC.

The columnar mesophases obtained for all these compounds are extremely viscous and appear similar in texture showing fan-shaped domains by polarising microscopy. Miscibility studies (by contact preparation) between the palladium (**2** and **3**) and platinum (**4** and **5**) compounds confirm that in each case, the mesophases obtained are of the same type. This mesophase was initially thought to be of columnar hexagonal type, however, further investigations with small angle X-ray scattering using **3a–c** and **5a** yield X-ray patterns which are characterised by large numbers of sharp reflections in the small angle region and a broad diffuse band in the wide angle region around 10°. The low angle Bragg reflections cannot be explained in terms of either a hexagonal or rectangular unit cell, but only on the basis of an oblique unit cell with parameters of *ca.* $a = 37$Å, $b = 23$Å and $\gamma = 70$–$75°$ independent of the bridging-halogen type and for *both* palladium and platinum compounds. In all cases, the molecules within the columns are disordered.

We have recently proposed a change to the naming conventions for the columnar phases displayed by these and other mesogens. Using traditional naming conventions, the columnar phases formed by these materials are denoted as D_{hd}, D_{rd} for discotic hexagonal and discotic rectangular phases respectively [25]. This does not, however accurately reflect the nature of the mesophase, describing the phase in terms of the structure of the component molecules rather than the overall phase architecture and composition of the mesogenic subunits; in these cases columnar stacks of flat, disc-like molecules.

To this end, and to bring the naming system in line with that for smectic and nematic phases, we propose that the phases be redesignated as Col_x in type where Col describes the columnar nature of the phase and x reflects the order within the phase (h, r, *ob* for hexagonal, rectangular and oblique respectively *etc*). Thus, the columnar oblique phase found in our compounds is named as $\mathrm{Col}_{ob,d}$; a columnar mesophase with oblique arrangement of mesogenic units within the lattice and the d subscript describing the disordered liquid-like organisation within the columns. The actual structure of the molecules contributing to the mesophase is not described and indeed it is not necessary to do so. This naming system could also encompass the octahedral metallomesogens described by Latterman and co-workers [26] and by Swager and Zheng [27] and designated as O_h and O_r although these materials have the complication of not being miscible with other columnar phases derived from disc-like materials.

The nematic columnar phases formed by our metallomesogens in mixtures with appropriate apolar organic solvents (see discussion of lyotropic mesomorphism later) are of lyotropic chromonic type which are related to the aqueous lyotropic nematic columnar phases of lath-like molecules [28, 29]. Here, the molecules form columnar structures which act as the mesogenic subunits. These phases are described as $\mathrm{N}_{\mathrm{chr},1}$ and $\mathrm{N}_{\mathrm{chr},2}$ which clearly describes the nematic-chromonic phase type in analogy to aqueous lyotropic nematic columnar N_c (from rod-like micelles) and nematic lamellar N_L [30] (composed of disc-like lamellar aggregates) and in contrast to the thermotropic N_D phase in which individual disc-like molecules constitute the mesogenic subunits. The final numeric subscript simply distinguishes between the two nematic phases found in our systems.

An interesting feature which emerges from the small angle X-ray studies of the tetra-metallomesogens [13, 14] is the temperature dependence of the lattice parameters of the columnar mesophase. As is usual, the molecular volume increases due to increasing mobility of the molecules with temperature. This increase of the molecular volume is accomplished by a slight decrease in the stacking period (*ca.* 0.25Å over 160°C) which is compensated for by a linear increase in the unit cell area along the xy-plane of the mesophase. However, the increase in the unit cell area is not coupled to a simple expansion along both principle axes $\vec{a}$ and $\vec{b}$; in increasing temperature the cell parameter $\vec{a}$ shows a slight *decrease* while a significant increase in observed for $\vec{b}$, there is no temperature dependence of γ, the angle between the two axes which remains close to 74°. Hence, on increasing temperature, the Col_{ob} phase structure is maintained and expands essentially only along the $\vec{b}$ axis of the unit cell. In general, increasing temperature and associated conformational disorder leads to a shortening of the repetition distance along the direction of mean alignment and to an enlargement in the perpendicular direction; the temperature dependence of the ratio $\vec{a}/\vec{b}$ indicates that the paraffinic density is greatest along the $\vec{a}$ direction.

As a model for this behaviour of our systems, it has been postulated that the central molecular cores are organised in rows along $\vec{b}$ with the director of the principle molecular axis oriented in a perpendicular direction. This allows for maximum interpenetration of the aliphatic chains of molecules in adjacent rows and provides a mechanism for the observed isotropic expansion of the unit cell with temperature.

The thermotropic behaviour of these series of complexes is surprisingly independent on the nature of the central core of the molecules. Moving from palladium to platinum metal or changing the nature of the halogen-bridges has very little effect on the thermotropic mesomorphism. This is not unexpected in view of their identical molecular structure and similar metal centred chemistry (the metals are analogous second and third row transition metals). Although differing inter- and intramolecular interactions might be expected to influence specific aspects of the mesophase behaviour as a direct function of molecular stacking, in practice variations in phase behaviour between the palladium and platinum complexes is minimal. We feel that this is clear evidence that mainly the periphery of the compounds control the mesophase properties in these materials, not the nature of the metal which plays a subsidiary role in these structures as a shape-template to form the desired molecular architecture.

LYOTROPIC MESOMORPHISM

All of the tetrametalorganyls (**2–5a–c**) show lyomesomorphism in apolar organic solvents (for instance in chloroform and long chain hydrocarbons). These have primarily been studied [24, 14–16] in binary mixtures with long chain alkanes solvents and show the formation of a viscous columnar phase and usually either one or two nematic columnar chromonic phases [12, 14] (a low temperature $N_{chr,1}$ and higher temperature $N_{chr,2}$). In examples showing only one nematic phase, this has been determined as the $N_{chr,2}$ phase.

Of interest from these lyotropic studies are the nature of the different mesophases formed, the influence of the length of the aliphatic chains *both* of the mesogens *and* the solvent used and the effect of the core (change in metal from palladium to platinum and the nature of the bridging groups) on the mesophase formation.

For the palladium series with dodecyloxy peripheral substituents, the chloride and bromide bridged complexes (**3a,b**) each display two different nematic phases, the iodo-bridged complex **3c**, in contrast shows only an ordered columnar phase. However, the specific effect of the bridging group is not well defined; incorporation of pseudo-halogen, thiocyanate bridging units also yields a nematic phase and for stilbenyl derived tetrapalladium analogues [11, 12] (with a longer imine–imine spacer unit), a nematic phase is observed for the chloro- and iodo-bridged complexes, but not for the bromo compound! Similarly, the only tetraplatinum organyl compound studied so far (**5a**) displays two nematic phases. [14] The two dimensionally ordered columnar lyotropic phase is observed for all the compounds in the high concentration region using contact preparations. This phase region shows no discontinuity with the thermotropic $\mathrm{Col}_{ob,d}$ phase and so can be considered as a swollen thermotropic columnar phase containing up to typically 20% excess solvent or alternatively as a chromonic M phase. The binary mixture phase diagrams of **3a** and **5a** with pentadecane are shown in Figure 3.

The phase diagrams show three basic phase regions, the swollen columnar area described above and two regions of different lyotropic nematic phases over a wide temperature and concentration range. The transition between the two nematic phases is indicated by changes in the Schlieren texture and a strong decrease in thermal fluctuations on heating from the

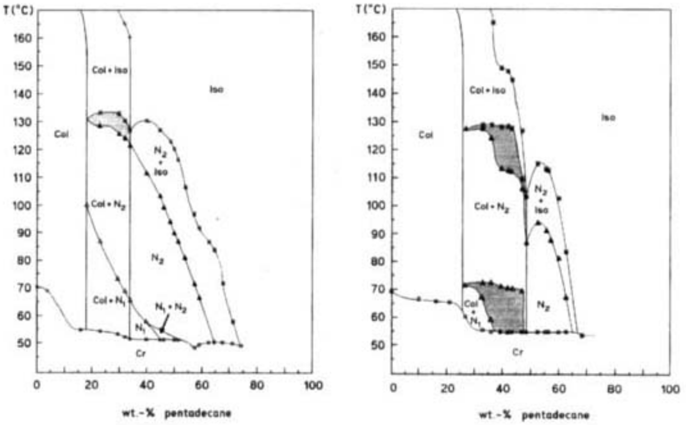


FIGURE 3 Lyotropic phase diagrams for the tetrapalladium and -platinum complexes **3a** (*left*) and **5a** (*right*), respectively in pentadecane [12, 14]. The shaded areas mark triphasic regions.

lower to upper nematic phase. This is in contrast to the usual observation of increasing thermal fluctuations with increasing temperature. The two phases are also indicated by orientational [31, 32], electro-optical [31, 32] and spectroscopic [16, 33] studies.

Using SiO_x coated cells with 60° deposition, the upper nematic phase shows homogeneous orientation. The molecules within the nematic phase are aligned perpendicular to the deposition plane. On cooling, the homogeneous planar orientation changes at the nematic–nematic transition temperature and shows two homogeneous domains separated by discontinuities and which show optical rotations of $\pm 33°$ relative to the upper nematic phase but with the optical axis of the mesophase still perpendicular to the deposition plane. That is, with the molecules tilted with respect to the director of the nematic phase.

Additional hints for the columnar structure of both nematic phases have been obtained from observations by polarizing microscopy while filling the cells used for the measurements above [31]. In the case of autonomous discs as the mesogenic units of the liquid crystal phase, the case for a N_D-phase, the director should be perpendicular to the surface of the cell and thus to the flow direction. For our metallomesogens **2**–**5** it is clear that the flat molecules flow into the cell in such a way that the director of the disc is arranged parallel to the flow direction. This behaviour is easily rationalised if the mesogenic unit is assumed to be a column with a reasonably high length to width ratio. This expectation is also supported by the following experiment; comparing the velocity of the flow into the cell with an attached external electrical field (oriented perpendicular to the cell) one detects a significant slower flow than in the case without an external field. Due to the negative dielectric anisotropy of our molecules the columns try to align parallel to the field. On flowing into the cell the columns (usually arranged parallel to the surface) now exhibit an angle with respect to the surface of the cell. Thus, the flowing "particles" have a larger effective diameter resulting in a slower flow.

The observation of a strong *bathochromic* shift in the uv spectra [16] of the metallomesogens (*ca.* 412–440 nm) on going from dilute solution to either nematic mesophase, $N_{chr,1}$ or $N_{chr,2}$ indicates than in both mesophases there is a significant degree of molecular aggregation which supports a columnar model for the nematic phases in contrast to a nematic discotic model comprising of discrete molecules.

The model proposed for the structures of the two mesophases which is in agreement with both the orientational measurements and the uv evidence for molecular aggregation in *both* nematic phases is with both phases composed of columnar arrays of molecules with a nematic ordering of the columns. In the lower temperature phase, the molecules are tilted with respect to the normal of the columns [12, 32] (the measured tilt angle is 44° from conoscopic measurements) whereas in the upper phase, the molecules are more usually oriented along the normal of the columnar stacks [34]. In both cases, the nematic phases can then be regarded are *chromonic* in nature and can be notated as $N_{chr,1}$ and $N_{chr,1}$ (see note [35]).

The tilted arrangement of discs within the columns of $N_{chr,1}$ describes a biaxial arrangement, however the mesophase shows *bulk* uniaxiality which can be ascribed to an arbitary orientational order between columns in the absence of an external applied field.

In general, coexistence of the two nematic phases is strongly influenced by the ratio of the lengths of the aliphatic chains of both the mesogen and the linear alkane solvent used. Both nematic phases are observed and stabilised when the length of the aliphatic chains of the solvent is broadly equal to, or slightly longer than those of the mesogen; using shorter chain solvents reduces the nematic polymorphism whereas significantly longer solvents inhibit formation of the nematic phases and only the viscous columnar phase is obtained.

Similarly, the overall length of the aliphatic chains in the compound is also important, the hexyloxy-substituted compounds display only sparse polymesomorphism; a *monotropic* nematic phase is observed when the solvent is pentane, hexane or heptane in addition to the $Col_{ob,d}$ phase whereas the analogous dodecyloxy-substituted compounds (with dodecane) display an *enantiotropic* nematic phase ($N_{chr,2}$) and a second monotropic nematic phase ($N_{chr,1}$) which is stabilised further as an enantiotropic phase with slightly longer length solvents (pentadecane–octadecane) [14, 31].

Of note is the observation that lyotropic phases are also obtained in binary mixtures with other, more polar solvents (for example, octanol, octadecanol and steric acid) which also resemble the thermotropic and lyotropic $Col_{ob,d}$ phases above.

In contrast to the significant effect that changing the length of the alkyl chains in either the mesogen or solvent has on the mesomorphism, changing the core of the mesogens (either the metal centres from palladium to platinum, or the bridging groups providing that the bridge remains planar) has only a minor effect on the thermo- and lyomesomorphism. In each case, changes to the mesomorphism are a direct effect of changing the intramolecular core–core stacking interactions, clearly the relative differences in these interactions on going from palladium to platinum and from chloride through bromide to iodide bridges is relatively small, however changing the spacer unit (from 1,4-phenylene to 4,4'-stilbenylene) leads to disappearance of the nematic polymorphism. Manipulation of the stacking interactions between molecules has a great effect on their mesomorphic properties, this is illustrated by the formation of *induced* mesophases, both thermotropic and lyotropic when the complexes are doped with small organic electron acceptors.

MESOPHASE INDUCTION BY DOPING WITH SMALL ORGANIC ELECTRON ACCEPTORS

Columnar mesophases may be induced or stabilisied by the formation of electron donor-acceptor or charge transfer complexes between the flat, sheet-like mesogens and organic electron acceptors (TNF or (±)-TAPA) [19] which increase the intramolecular columnar stacking interactions and form columns in which the electron acceptors are intercalated within the columnar stacks. The assembly of supramolecular stacks leads to stabilisation or induction of mesophases [18].

For the bis-metallomesogens **6** and **7** formation of electron donor-acceptor complexes induces the formation of enantiotropic $\mathrm{Col}_{h,o}$ phases in which the columns are close-packed in a hexagonal array and within the columns, the molecules are ordered which is in contrast to the largely liquid like organisation of the molecules in the neat monotropic N_D phase of the pure mesogen. Similarly, for the tetrametallomesogens **2**–**5**, complexes with TNF [19] yield stabilised $\mathrm{Col}_{h,o}$ mesophases with a higher degree of order, especially within the columns than in the parent $\mathrm{Col}_{ob,d}$ mesophases [14].

Furthermore, charge-transfer induced/stabilised *lyotropic* mesophases have also been found. For the tetrametallomesogens, ternary mixtures with TNF and organic solvents show stabilisation of a $\mathrm{N}_{\mathrm{chr}}$ mesophase [12, 16], which might be anticipated to show increased intercolumnar order although this has not yet been determined. Similarly, when chiral electron acceptors ((+)-or (−)-TAPA) [19] are used as dopants, cholesteric nematic phases ($\mathrm{N}^*_{\mathrm{chr}}$) are obtained [14, 15]. These show an increase in helical pitch with increasing temperature which is similar to that found in aqueous miscellar nematic systems [36].

CONCLUSIONS

The family of metallomesogens described here differ in their general mesomorphic behaviour from the related materials prepared for example by

Espinet and co-workers [5, 7]. Despite a similar chemical structure, the overall topology of our materials is different, being flat, sheet-like as opposed to a general H-shaped twinned-calamitic form. This change in overall shape may be effected using two complementary routes; (i) obtaining a different peripheral substitution pattern [8, 10], in this case by addition of lateral substituion which perturbs the initial rod-like structure of the ligands and (ii) modification of the imine ligands to allow bis-metallation on each ligand [8, 11, 13, 14] which, as we have shown, leads in a novel kind of metal induced "dimerisation" to large flat and macroheterocyclic tetrametallated compounds as a result of a metal-centred self-assembly process. Thus we have two different strategies which may be combined for the manipulation of the structure and mesomorphic properties of these multimetallomesogens. The actual mechanism for the metal induced macrocyclisation which forms exclusively tetrametalloheterocycles as opposed to polymeric oligomers has not yet been completely explored although clearly, the relatively high yields for the palladium cyclometallations indicate that the driving force for this unique "dimerisation" is high.

The thermotropic and lyotropic properties of the compounds are controlled by the nature of the ligands, in particular the nature and distribution of substitutents around the periphery of these interesting organyls. Although the metal centres and bridging groups have an important role in the assembly of the compounds with the correct topology, the nature of the metal beyond a requirement to adopt a square-planar geometry appears to have little influence on the mesomorphism.

Thermotropic nematic discotic and columnar mesophases are obtained with additional nematic chromonic lyotropic phases in apolar organic solvents for these metallomesogens; their range and stability is influenced both by the ligand substitution and by the solvent. Importantly, two nematic phases occur as a general phenomena. Chemical manipulation of the thermotropic and lyotropic mesophases by addition of intercalating electron acceptor dopants stabilises the columnar stacking interactions and leads to more ordered phases and can, in some instances lead to induced mesophase formation, *e.g.* the lyotropic chiral chromonic (N^{*}_{chr}) phase [14, 15].

The wide range of mesomorphism displayed by our compounds and the modifications of their properties possible by simple structural manipulation, solvent or addition of dopants should help contribute to an improvement in our knowledge of liquid crystal systems; especially in the distinction between 'rods' and 'discs'. With regard to this, and in view of the large range of possible liquid crystal phases that may be possible in such systems (for example, hexagonal, rectangular, oblique, nematic organisation of columnar aggregates with ordered, disordered or tilted molecular arrangement within a column) we suggest that the labelling of such columnar mesophases should be changed to reflect supramolecular rather than molecular structure.

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References

[1] Part 94 of liquid crystalline compounds; part 93: M. Langner,, K. Praefcke, G. Heppke, and K. Krüerke, *J. Mater. Chem.*, **5**, 693 (1995).

[2] Reviews by (i) L. Oriol and J. L. Serrano, *Adv. Mater.*, 1995, **7**, 348; (ii) Hudson, S.A. and P. M. Maitlis, *Chem. Revs.*, 1993, **93**, 861; (iii) A. P. Polishchuk and T. V. Timofeeva *Russ. Chem. Revs.*, 1993, **62**, 291; (iv) D. W. Bruce, *J. Chem. Soc., Dalton Trans.*, 1993, 2983; (v) D. W. Bruce, in *Inorganic Materials*, eds D. W. Bruce and D. O. Hare, Wiley, Chichester, 1992; (vi) P. Espinet,, M. A. Esteruelas, L. A. Oro, J. L. Serrano and E. Sola, *Coord. Chem. Rev.*, 1992, **117**, 215; (vii) A.-M. Giroud-Godquin and P. Maitlis, *Angew. Chem., Int. Ed. Eng.*, 1991, **30**, 402.

[3] P. M. Maitlis, M. J. H. Russell and P. Espinet, (1982) Vol 6 Chapters 38.1–38.9 and F. R. Hartley, Vol 6, Chapter 39, in *Comprehensive Organometallic Chemistry*, ed G. Wilkinson, Pergammon , Oxford, 1982.

[4] M. Ghedini, M. Longeri and R. Bartolino, *Mol. Cryst. Liq. Cryst.*, **84**, 207 (1982).

[5] J. Barbera, P. Espinet, E. Lalinde, M. Marcos and J. L. Serrano, (1989) *Liq. Cryst.*, 1987, **2**, 833; (ii) P. Espinet, J. Etxebarria, M. Marcos, J. Perez, A. Remon and J. L. Serrano, *Angew. Chem.*, Int. Ed. Engl., **28**, 1065 (1989).

[6] M. Ghedini, D. Pucci, G. de Munno, A. Crispini and F. Neve, *Chem. Mater.*, **3**, 65 (1991).

[7] M. B. Ros, N. Ruiz, L. Serrano and P. Espinet, *Liq. Cryst.*, **9**, 77 (1991).

[8] K. Praefcke, D. Singer and B. Gündoğan, (1992) *Mol. Cryst. Liq. Cryst.*, **223**, 181, and prior poster presentations, summarised here in ref. 1, from 1990.

[9] K. Praefcke, B. Bilgin, J. Pickardt and Borowski, M. (1994) *Chem. Ber.*, **127**, 1543.

[10] B. Kohne and K. Praefcke, *Chem.-Ztg.*, **109**, 121 (1985).

[11] B. Gündoğan and K. Praefcke, *Chem. Ber.*, **126**, 1253 (1993).

[12] N. Usol'tseva, K. Praefcke, D. Singer and B. Gündoğan, *Liq. Cryst.*, **16**, 601 (1994).

[13] K. Praefcke, S. Diele, J. Pickardt, B. Gündoğan, U. Nütz and D. Singer, *Liq. Cryst.*, 1995, **18**, 857; for **2b** see the Ph.D. thesis of D. Singer, Fachbereich 5 /Chemie, Technische Universität Berlin, 1994; ISBN 3-929937-79-4, Verlag Köster, 12307 Berlin.

[14] K. Praefcke, B. Bilgin, N. Usol'tseva, B. Heinrich and D. Guillon, *J. Mater. Chem.*, **5**, 2257 (1995).

[15] N. Usol'tseva, K. Praefcke, D. Singer and B. Gündoğan, *Liq. Cryst.*, **16**, 617 (1994).

[16] N. Usol'tseva, K. Praefcke, D. Singer and B. Gündoğan, *Mol. Mater.*, **4**, 253 (1994).

[17] D. Singer, A. Liebmann, K. Praefcke and J. H. Wendorff, *Liq. Cryst.*, **14**, 785 (1993).

[18] K. Praefcke and D. Singer, *Mol. Mater.*, **3**, 265 (1994).

[19] 2,4,7-Trinitrofluorenone and (+)- or (−)-2-(2,4,5,7-tetranitro-9-fluorenylideneaminoxy) Propionic acid, respectively.

[20] J. M. Vila, M. Gayoso, T. Pereira, C. Rodriguez, J. M. Ortigueira and M. Thornton-Pett, *J. Organomet. Chem.*, **426**, 267 (1992).

[21] K. Praefcke, B. Kohne, B. Gündoğan, D. Singer, D. Demus, S. Diele, G. Pelzl and U. Bakowsky, *Mol. Cryst. Liq. Cryst.*, **198**, 393 (1991).
For a discussion of the interesting mesomorphic properties of the ligands itself *cf.* this reference.

[22] Due to the lack of acetato bridged platinum compounds, here no comprehensive studies could be done. Therefore the thermal behaviour and the mesogenic properties of the corresponding palladium compounds are not discussed here either.

[23] D. J. Mabbott, B. E. Mann and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 294 (1977).

[24] For the Pd series: Prof. J. Pickardt, Faculty 5/Chemistry, Technische Universität Berlin, private communication.

[25] C. Destrade, N. H. Tinh, H. Gasparoux, J. Malthête and A. M. Levelut, *Mol. Cryst. Liq. Cryst.*, **71**, 111 (1981).

[26] S. Schmidt, G. Latterman, R. Kleppinger and J. H. Wendorff, *Liq. Cryst.*, **16**, 693 (1992).

[27] T. M. Swager and H. Zheng, *Mol. Crysts. Liq. Cryst.*, **260**, 301 (1995).

[28] T. K. Attwood, J. E. Lydon and F. Jones, *Liq. Cryst.*, **1**, 499 (1986).

[29] T. K. Attwood, J. E. Lydon, C. Hall and G. J. T. Tiddy, *Liq. Cryst.*, **7**, 657 (1990).

[30] L. Yu and A. Saupe, *J. Amer. Chem. Soc.*, **102**, 4879 (1980).

[31] G. Hauck, H. D. Koswig, N. Usol'tseva, K. Praefcke and B. Heinrich, poster presentation (P45) at the 24. Freiburger Arbeitstagung Flüssigkristalle, Freiburg, Germany, 5–7 April 1995.

[32] N. Usol'tseva, H. D. Koswig, G. Hauck, K. Praefcke and B. Heinrich, *Liq. Cryst.*, **20**, 731 (1996).

[33] Private communications on results from ^{2}H-NMR studies by G. R. Luckhurst, University of Southampton, U.K., and D. Singer and Z. Luz, The Weizmann Institute of Science, Israel, from June and September 1995, respectively.

[34] For a pictorial representation of similar organisation see figure 6 of Ibn-Elhaj, M., D. Guillon, A. Skoulios, A. M. Giroud-Godquin and P. Maldivi, *Liq. Cryst.*, **11**, 731 (1992).

[35] Since recent measurements (ref. 31) show that the molecules are tilted within the lower nematic phase and are disordered in the upper nematic phase, the two phases could be labeled more thoroughly as $N_{chr,t}$ and $N_{chr,d}$, respectively, though we retain the subscripts, 1 and 2, to provide a link to previous work where the two phases had not yet been unambiguously identified.

[36] K. Radley, *Liq. Cryst.*, **11**, 753 (1992).