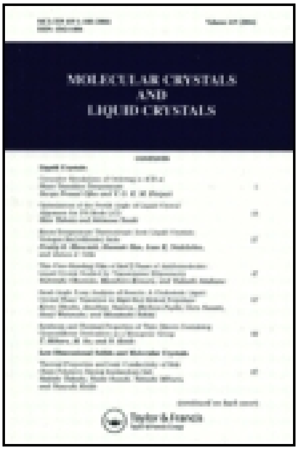

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Flat Mesomorphic Metal Organyls

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FLAT MESOMORPHIC METAL ORGANYLS[1]

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Abstract Large-sized flat tetrametallomesogens containing palladium or platinum in their macroheterocyclic cores show wide ranging liquid crystalline properties, both thermotropic and lyotropic in apolar organic solvents. Here, we briefly summarise recent work from our laboratory concerning these novel metallomesogens and related bis-metal analogues.

INTRODUCTION

Metal containing liquid crystals (metallomesogens) are growing in importance, for an overview see the seven reviews[2] which have appeared since 1991. Their attraction rests with 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 academic and commercial interest and have become a current subject in liquid crystal research primarily as cyclopalladated azobenzene,[4] diarylazine,[5] phenylpyrimidine[6] and most importantly in the context of our work since about 1990, arylimine[7] complexes (figure 1). These materials[4–7] typically have a *bis*-metallic **H**-shaped *twinned-rod* structure, or are *mono*-metallic **P**-shaped complexes with the bridging ligands replaced by acetylacetonate and display mesophases typical of calamitic liquid crystals (*i.e.* smectic and nematic phases) consistent with their rod-like structures.

In contrast, we have prepared *bis*-palladium arylimine complexes[8] (**1**) and more recently the first examples of analogously cyclo*platinated* metallomesogens[9] (**2**) which, though possessing the same or related cores as those from other research groups in figure 1[4–7] contain *additional* lateral substituents (shown as highlighted ether functions in our examples in figure 1) and therefore, now display mesophases characteristic of *flat*, *sheet*-like materials. These compounds are interesting since they are examples where the same type of metal coordination core yields both rod- and sheet-like shapes depending on peripheral substitution pattern.[10]

We first looked at the effect of peripheral substitution on the mesomorphic properties of organic materials in general over ten years ago[11] and since our first report

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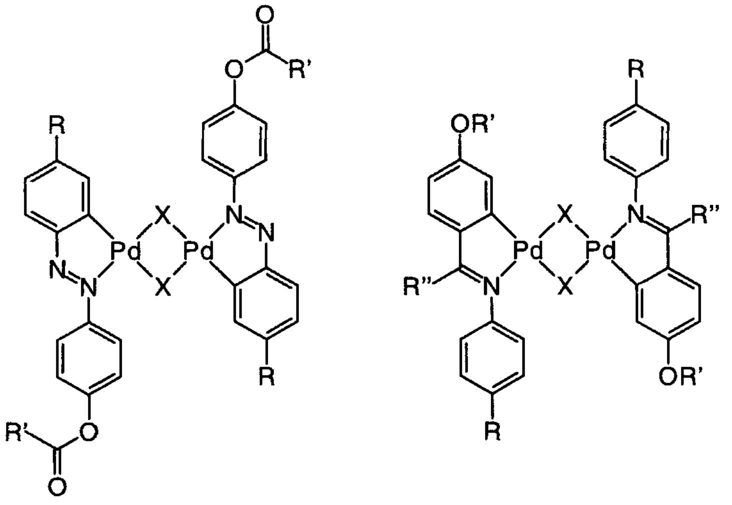
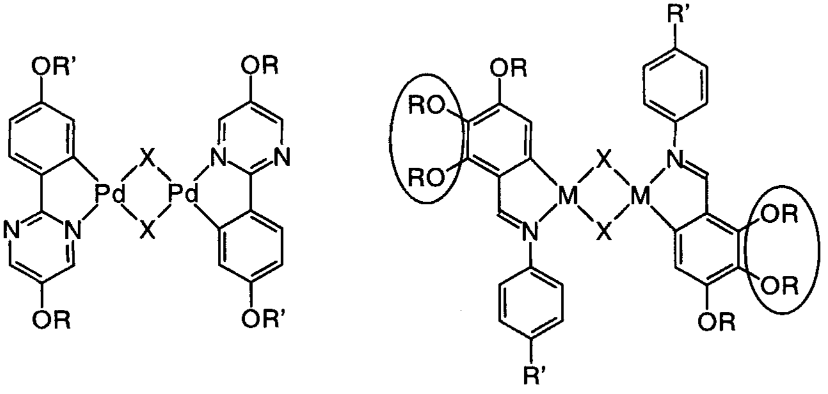


M. GHEDINI et. al., ITALY, 1982

X = Cl,Br,I

P. ESPINET et. al., SPAIN, 1991

X = Cl,Br,I



M. GHEDINI et. al., ITALY, 1991

X = Cl,Br,I

Our laboratory,

M = Pd (1992) or

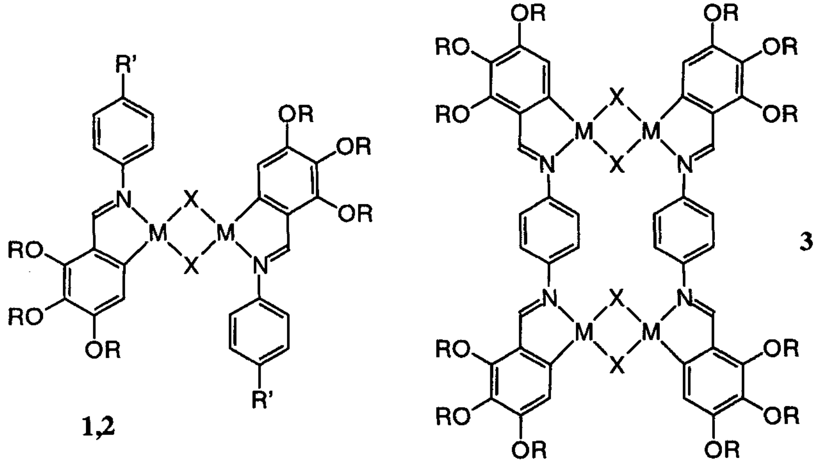
Pt (1994)

X = Cl,Br,I,SCN,N_3

FIGURE 1 The basic structural motifs of cyclometallated dinuclear mesogens (R,R'=long alkyl chains, R''=H or 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[10] from calamitic (mostly smectic) observed for the other examples to discotic (N_D).

of di- and tetrapalladium *bis*-mono and -diimine complexes, respectively, some six years ago,[8] we have become increasingly interested in the influence that the peripheral substitution, the bridging ligand and the metal atom type have on the mesomorphism of these systems. It has been suggested[2(ii)] that our flat metal organyls are close to a "calamitic/discotic crossover point" and might be anticipated to show mesogenic behaviour with some characteristics of each phase type, in particular the possibility of biaxiality and associated fast switching effects.

Here, we provide a perspective on recent work in our laboratory centred on the investigation of multipalladium[8,12–14] and -platinum[9,15] sheet-like materials (**1–6**, figure 2), in **3–6** with central metallomacroheterocycles. These have wide ranging liquid crystalline mesomorphism, both thermotropic and also lyotropic[13,15–17] in apolar organic solvents including two lyotropic nematic columnar phases side by side and also interesting *induced* mesophase formation[1,17–19] in the presence of small organic electron acceptors *i.e.* TNF (2,4,7-trinitrofluorenone) or TAPA ((+)- or (–)-2-(2,4,5,7-tetranitro-9-fluorenylideneaminoxy) propionic acid).



1,2

3-6

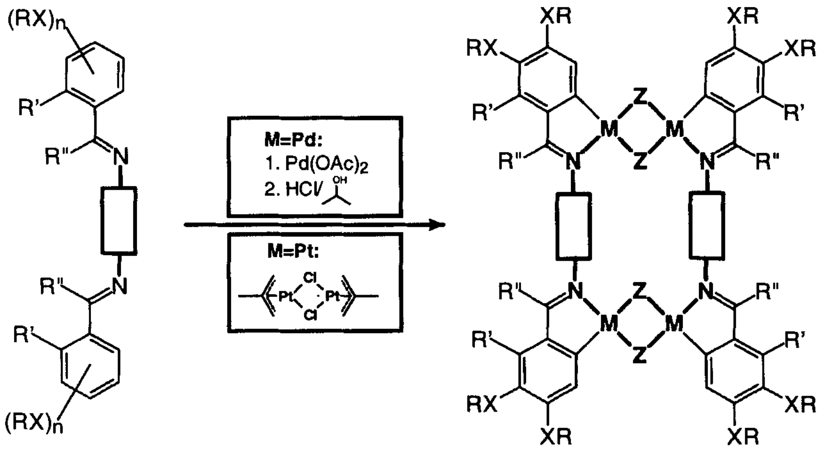
	M	R	X
1	Pd	C_6H_{13}	**a**: Cl, **b**: Br, **c**: I
2	Pt	C_6H_{13}	**a**: Cl

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

FIGURE 2 Some of the bis- (**1,2**)[8,9] and tetrametallomesogens (**3–6**)[8,14,15] introduced and studied in our laboratory (M=Pd or Pt, X=halogen and R,R'=various long alkyl groups).

SYNTHESIS

The metalorganyls **1**–**6** (figure 2) are obtained by ortho-cyclometallation of the respective imines (prepared from 2,3,4-tri(alkyloxy)derivatives of benzaldehyde and aromatic mono- or diamines) with either palladium acetate or di-μ-chloro-bis-(η^3-2-methylallylplatinum)[20] and subsequent bridging group substitution[8,9,12,14,15] as shown for bis-imines (**A**) in figure 3 which cleanly yield the "dimeric" tetrametalorganyls of type **B** for which **3**–**6** in figure 2 are four mesomorphic examples prepared by us. It is interesting to note that oligomers are not formed in these reactions.[8,12,14,15,21]



A **B**

FIGURE 3 Illustration of the easy synthetic access to the flat tetrametallomesogens of type **B**, series **3**, with their unique and different macroheterocyclic units as central oval 'molecular windows' [M=Pd or Pt; R,R'=long alkyl: R'=H (R''=R) or RX (R''=H); X=oxygen or sulphur; Z=halogen, N$_3$ or SCN; —☐— =phenyl, biphenyl, stilbenyl or p-terphenyl], in part still unpublished.

X-ray diffraction studies[14,21] of two tetrapalladium derivatives of type **B**, series **3**, show that the planarity and overall geometry of the metallomacroheterocyclic central 'molecular window' is preserved independently of the nature of the halogen bridges and presents a large flat metallo-aromatic core with twelve alkoxy substituents arranged around the periphery. The dinuclear metallomesogens **1** and **2** (figure 2) display anti-parallel orientation of the imino ligands shown by NMR[8] and single crystal X-ray scattering.[9]

THERMOTROPIC PHASE BEHAVIOUR

The four *bis*-metallated complexes **1a–c**[8] and **2a**[9] melt between about 79–98°C and show a monotropic nematic discotic (N_D) phase on cooling to about 44–27°C. These compounds were the first examples of cyclometallated metallomesogens forming this type of phase in contrast to calamitic phases[4–7] and indicate that control of the peripheral substitution pattern provides a good mechanism for strong influence on the phase behaviour.

The twelve tetrametallated compounds **3–6** each display enantiotropic columnar mesophases; the mesomorphism of two representative tetracyclometallated organyl series with either palladium or platinum, halogen-bridges (X=Cl, Br, I) and either twelve hexyloxy (**3a–c**, **5a–c**) or dodecyloxy-chains (**4a–c**, **6a–c**) around the periphery of the molecules is shown in table 1.

TABLE 1 Thermotropic phase transition temperatures (°C, approximated to the nearest degree) for the tetrapalladium (**3a–c**, **4a–c**)[8,14] and -platinum (**5a–c**, **6a–c**)[15] liquid crystals, *cf.* figure 2; Cr: crystalline, Col_{ob}: columnar oblique mesophase, Iso: isotropic liquid, and dec.: decomposition.

	M	R	X	Cr		Col_{ob}		Iso	
3a	Pd	C_6H_{13}	Cl	●	332	—		●	dec.
b			Br	●	103	●	306	●	dec.
c			I	●	123	●	306	●	dec.
4a	Pd	$C_{12}H_{25}$	Cl	●	71	●	301	●	dec.
b			Br	●	69	●	279	●	dec.
c			I	●	62	●	265	●	dec.
5a	Pt	C_6H_{13}	Cl	●	100	●	357	●	dec.
b			Br	●	111	●	341	●	dec.
c			I	●	107	●	328	●	dec.
6a	Pt	$C_{12}H_{25}$	Cl	●	70	●	280	●	dec.
b			Br	●	68	●	292	●	dec.
c			I	●	55	●	297	●	dec.

The temperature range of the columnar mesophases is in all cases large (> 200° C);[8,14,15] the dodecyloxy analogues (**4a–c**, **6a–c**) have slightly lower transition temperatures than the corresponding hexyloxy derivatives (**3b–c**, **5a–c**). The chloro-bridged tetrapalladium compound (**3a**) unusually shows no liquid crystal mesomorphism melting at 332°C.

The columnar mesophases obtained are extremely viscous and similar in texture showing fan-shaped domains by polarising microscopy. Miscibility studies between the palladium (**3** and **4**) and platinum (**5** and **6**) compounds confirm that the mesophases obtained are of the same columnar type which was initially thought to be columnar hexagonal. Investigations with small angle X-ray scattering using **4a–c** and **6a** reveal an oblique unit cell which is independent of the bridging halogen type and the metal centres. In all cases, the molecules within the columns are disordered.

The unit cell shows temperature dependent expansion[14,15], essentially only along the $\vec{b}$ axis. This indicates that the paraffinic density is greatest along the $\vec{a}$ direction and as a model for this behaviour, it has been postulated[15] that the molecular cores are organised in rows along $\vec{b}$ with the director of the principle molecular axis oriented in a perpendicular direction which allows for maximum interpenetration of the aliphatic chains of molecules in adjacent rows and provides a mechanism for the observed isotropic thermal expansion of the unit cell.

The thermotropic behaviour of these series of complexes is surprisingly independent on the nature of the core of the molecules. Moving from palladium to platinum or changing the nature of the halogen-bridges has very little effect on the thermotropic mesomorphism. Although differing inter- and intramolecular interactions might be anticipated 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. The nature of the metal plays a subsidiary role in these structures, acting primarily as a shape-template to form the desired molecular architecture.

We have recently proposed a change to the naming of the columnar phases displayed by these and other mesogens.[15,22] Using the conventional naming, the columnar phases formed by such materials are denoted as D_{hd} and D_{rd} for the columnar hexagonal and rectangular phases, respectively.[23] However, we feel that the common use of the letter D for such designations can lead to confusion and the mistaken conception that the *mesophases* are actually discotic rather than being *columnar* in nature, obtained from disk-like or more generally flat, sheet-like mesogens.

In order to present a phase labelling which helps to reflect the phase structure more effectively and reduces this potential for confusion, we suggest that the phases –*cf*. table 1– be redesignated as Col_x in type where 'Col' describes the columnar nature of the phase and x reflects the order within that 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.

LYOTROPIC MESOMORPHISM

All the metal complexes, **1**–**6**, show lyomesomorphism in apolar organic solvents (for instance in chloroform or long chain hydrocarbons). For the tetrametalorganyls **3**–**6**, these have been studied[13,15–17] in binary mixtures with long chain alkane solvents and show the formation of a viscous columnar phase and either one or two nematic columnar phases of chromonic type[13] (a low temperature $N_{chr,1}$ and a higher temperature $N_{chr,2}$) which are described in analogy to the aqueous lyotropic nematic columnar phases of lath-like molecules.[24] In examples showing only one nematic phase, this has been determined as the $N_{chr,2}$ phase.

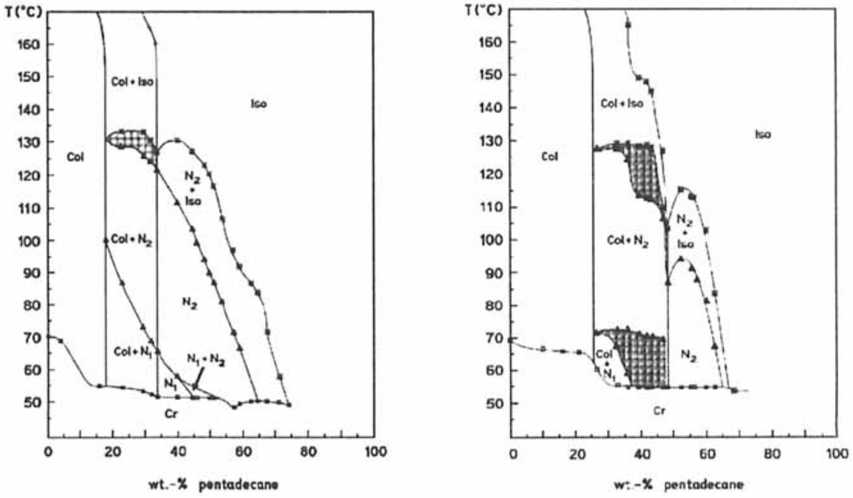


FIGURE 4 Lyotropic phase diagrams for the tetrapalladium and -platinum complexes **4a** (*left*) and **6a** (*right*), respectively, in pentadecane.[13,15] The shaded areas mark triphasic regions.

For the tetrapalladium series with dodecyloxy peripheral substituents, the chloride and bromide bridged complexes (**4a,b**) each display two nematic phases; the iodo-bridged complex **4c**, in contrast shows only an undefined type of two-dimensionally 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[12,13] (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 studied so far, the chloro-bridged compound (**6a**) displays two nematic phases.[15] The binary mixture phase diagrams of **4a** and **6a** with pentadecane are shown in figure 4.

The high concentration lyotropic two-dimensionally ordered columnar phase is observed in a continuum with the thermotropic $\mathrm{Col}_{ob,d}$ phase, this can be considered as a swollen thermotropic columnar phase containing up to typically 20% excess solvent and can probably also be described as a chromonic M phase.[13]

The nature of two lyotropic nematic phases (found over wide temperature and concentration regions) have prompted interest. For instance orientational[25,26], electro-optical[25,26] and spectroscopic[17,27] studies show that *both* nematic phases are composed of columnar arrays with a nematic ordering of the columns. In the lower temperature phase ($\mathrm{N}_{chr,1}$), the molecules are tilted with respect to the normal of the columns.[13,26] This tilted arrangement of sheets within the columns of $\mathrm{N}_{chr,1}$ describes a biaxial situation, however, the mesophase shows *bulk* uniaxiality which can be ascribed to an arbitary orientational order between the columns in the absence of an external applied field. In the upper phase ($\mathrm{N}_{chr,2}$), the molecules are more usually oriented along the normal of the columnar stacks.

The coexistence of these two nematic phases is strongly influenced by the ratio of the length of the aliphatic chains (the 'internal' solvent) of the mesogen and the linear alkane used. Both nematic phases are observed when the length of the aliphatic chains of the alkane solvent is broadly equal to, or slightly longer, than that 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.

The overall length of the aliphatic chains in these compounds is also important, for example, the *hexyl*oxy-substituted tetraplatinum organyl displays only sparse polymesomorphism; simply a *monotropic* $\mathrm{N}_{chr,2}$ phase is observed in addition to the $\mathrm{Col}_{ob,d}$ phase when the solvent is pentane, hexane or heptane whereas the analogous dodecyloxy-substituted mesogen (with dodecane) displays an *enantiotropic* $\mathrm{N}_{chr,2}$ phase and a *monotropic* $\mathrm{N}_{chr,1}$ phase which becomes enantiotropic with slightly longer solvents (pentadecane–octadecane).[15,25,28]

Lyotropic phases are also obtained in binary mixtures with other, more polar solvents, for example, octanol, octadecanol and stearic acid.[13]

Changing the spacer groups (from 1,4-phenylene to 4,4'-stilbenylene) leads to the disappearance of the nematic polymorphism, whereas changing the metals (*i.e.*, between palladium and platinum) has only a minor effect on the thermo- and lyomesomorphism.

INDUCTION OF MESOPHASES

Columnar mesophases can be induced or stabilised by the formation of donor-acceptor complexes between the sheet-like molecules and organic electron acceptors (for instance, TNF or (±)-TAPA, see above) which increase the intramolecular stacking interactions.[1,19]

In the case of the bis-metallomesogens **1** and **2**, formation of electron donor-acceptor complexes with TNF induces the enantiotropic $\mathrm{Col}_{h,o}$ phase with the columns close-packed in a hexagonal array. Similarly, for the tetrametallomesogens **3–6**, complexes with TNF yield stabilised $\mathrm{Col}_{h,o}$ mesophases with a higher degree of order than in the parent $\mathrm{Col}_{ob,d}$ mesophases.[15]

Furthermore, charge-transfer induced/stabilised *lyotropic* mesophases have also been found. For both the bis- and tetrametallomesogens, ternary mixtures with TNF and a linear alkane show stabilisation of the $\mathrm{N}_{chr,2}$ mesophase.[1,13,17] Similarly, when chiral electron acceptors ((+)- or (−)-TAPA) are used as dopants, cholesteric nematic phases (N^*_{chr}) are obtained.[15,16] These show an increase in helical pitch with increasing temperature[16] which is similar to that found in aqueous micellar nematic systems.[29]

CONCLUSIONS

The bis-metallomesogens (**1**,**2**) differ in their general mesomorphic behaviour from the related materials prepared by other research groups,[4–7] now showing *nematic discotic* rather than mainly smectic mesophases. Despite a similar core chemical structure, the overall topology of our materials is different, being flat, sheet-like as opposed to a general **H**-shaped twinned-calamitic form. Also, the tetrametalorganyls (**3-6**) have a large, flat overall shape but display *columnar* mesophases. This change in shape towards that of our compounds may be obtained using two complementary routes: (i) obtaining a different peripheral substitution pattern,[8,11] in this case by additional lateral substitution to compounds **1** and **2** which perturbs the initial rod-like structure of the ligands and (ii) by modification of the imine ligands in **3-6** to allow bis-metallation on each ligand which, as it was shown,[8,12,14,15,21] leads in a novel kind of metal induced "dimerisation" to large flat and macroheterocyclic tetrametallated compounds as a result of a metal-centred square-planar 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. It is interesting to note that the tetrametalorganyls **3–6** are the heaviest low molecular weight mesogens known.

The thermotropic and solvent dependent lyotropic properties of these multimetalorganyls are controlled by the nature of the ligands, in particular the type and distribution of substituents around the periphery of these interesting liquid crystals. Although the metal centres and bridging groups have an important role in the assembly of these 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 their mesomorphism. Therefore, it can truely be said that here *"ligands make mesogens"*.[10]

Thermotropic nematic discotic and columnar mesophases and in addition various chromonic lyotropic phases in long-chain organic solvents are obtained for these interesting metallomesogens. Of importance is the (so-far) unique observation of two lyotropic nematic phases which occur side by side in systems of sheet-like molecules. 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 including, *e.g.*, the lyotropic chiral chromonic (N^*_{chr}) phase.[15,16]

The wide range of mesomorphism displayed by our metal organyls combined with the modification to their properties possible by simple structural manipulation or the addition of dopants and/or solvent should help contribute to an improvement in our knowledge of liquid crystal systems. With regard to this, and in view of the large range of 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 the supramolecular rather than molecular structure.[15,22]

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