

Metallomesogens by ligand design †

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In this Perspective, some of the basic principles of ligand design will be described as they apply to the synthesis of metal complexes with liquid crystal properties. Liquid crystal properties of metal complexes are a delicate function of both ligand and metal and examples will be chosen to illustrate this statement. In particular, the effect of the metal complex moiety on the mesomorphism of a series of imine and diimine liquid crystals is described.

Introduction

Liquid crystals based on metal complexes (metallomesogens) have been known since the early part of the 20th century, but they were clearly regarded as curiosities as reports of their synthesis and properties were sporadic until the early 1980s. The renaissance of the subject is often and properly ascribed to a publication by Giroud and Mueller-Westerhoff in 1977,¹ in which they reported the synthesis and liquid crystal properties

of some Ni(II) dithiolenes (Fig. 1). In the context of the current article, this is most appropriate as they had designed their metal–ligand combination in a rather specific manner. Thus, they proposed that the central metal–dithiolenone unit might be considered equivalent to a phenyl ring and thus the complex could be considered as being a structural analogue of a 4,4'-dialkylterphenyl (which has liquid crystal properties). Since then, the subject has grown hugely and has been the subject of several reviews² and a book.³

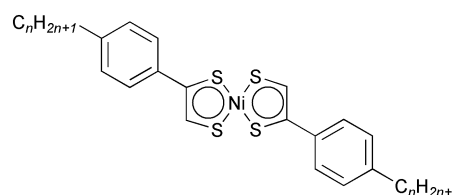


Fig. 1 Mesomorphic nickel(II) dithiolenone complexes.

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This article seeks to take a number of examples from the metallomesogen literature to try to exemplify how the demands

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Richard Date



Eva Fernandez Iglesias

Eva Fernandez Iglesias was born in Oviedo, Spain. She graduated in Chemistry at the University of Oviedo in 1999 after completing her final year at the University of Exeter under an ERASMUS agreement. She stayed in Exeter to complete her Ph.D. with Professor Duncan Bruce, graduating in 2002. She now works in the chemical industry in the south-west of England.



Duncan Bruce

Duncan Bruce graduated from the University of Liverpool in 1981 and remained there for his Ph.D. under the supervision of David Cole-Hamilton, during which time he studied phosphine complexes of Pt(II) and Rh(I) as potential photocatalysts for the decomposition of water. In 1984, he took up a Temporary Lectureship in Inorganic Chemistry at the University of Sheffield and, in 1986, was awarded a Royal Society Warren Research Fellowship, which he held there until 1991. He was then appointed Lecturer in Chemistry and was promoted to Senior Lecturer in 1994, in which year he became co-director of the Sheffield Centre for Molecular Materials. In 1995, he was appointed Professor of Inorganic Chemistry at the University of Exeter, the position he now holds. Professor Bruce has research interests in different aspects of materials chemistry, central to which is an abiding passion for the materials chemistry of coordination compounds and, in particular, their liquid crystal properties. He was awarded the first Young Scientist prize by the British Liquid Crystal Society in 1990, was RSC Sir Edward Frankland Fellow in 1994/95 and was awarded one of the Corday-Morgan Medals and Prizes in 1996. He was a founding member of the RSC's Materials Chemistry Forum and is a former member of the Dalton Council.

of liquid crystal design may be met, and also challenged, by metal–ligand combinations. In order to make this article self-contained, a brief introduction to liquid crystals will be given here.

A brief introduction to liquid crystals

The liquid crystal state (known as a *mesophase*) represents a discrete state of matter which exists between the solid and liquid states; like a liquid it is fluid and yet like a solid, it has order. This combination of order and fluidity results in mesophases with anisotropic physical properties and it is these which have led to their widespread application in, for example, low-power-consumption displays. Liquid crystals are first classified according to the method used to destroy the order of the solid state, of which there are two possibilities. In *lyotropic* liquid crystals, this order is destroyed by the action of solvent, perhaps in conjunction with heat, and typical examples of mesomorphic materials would include amphiphilic materials, certain polymers or disk-like materials with highly polar peripheries.⁴ Such materials will not be considered further.

In *thermotropic* liquid crystals, however, transitions between the solid, liquid and liquid crystal states are effected by the action of temperature and, on heating, a typical material might show transitions from solid to liquid crystal to isotropic liquid (the adjective ‘isotropic’ is added in recognition of the fact that the liquid crystal is an anisotropic liquid). Transitions between the solid state and mesophases are typically strongly first order from a thermodynamic point of view and often supercool, while transitions between a mesophase and the isotropic liquid are weakly first order. Transitions between mesophases are either weakly first order or, occasionally, second order. The single most important criterion for the formation of liquid crystal mesophases is that the molecules should be structurally anisotropic for this introduces additional, anisotropic dispersion forces between the molecules which are strong enough to stabilise the mesophase. In the context of this article, this anisotropy can be a delicate interplay of metal and ligand.

Within thermotropic liquid crystals, there are many classifications according to shape and also, occasionally, the mesophases that they form. For many years, only two classifications were necessary, namely calamitic (rod-like) and discotic (disk-like), as this effectively described most, if not all, of the known mesogens. However, in addition we now have to take into account other structural motifs such as bowlic liquid crystals,⁵ dendrimeric mesogens,⁶ polycatenar mesogens⁷ and bent-core mesogens.⁸ To help the first-time reader in the subject, it may be helpful also to know that the term *mesogenic* refers to something which is ‘liquid-crystal like’ but which does not necessarily

have to have liquid crystal properties. However, something which is *mesomorphic* actually shows liquid crystal behaviour.

Nematic mesophases

The nematic phase (abbreviated, N) is the most disordered type of liquid crystal mesophase, and in the context of thermotropic liquid crystals, we will identify three types of nematic phase, namely that derived from rod-like molecules and two derived from disk-like molecules. In the first (Fig. 2a), the phase comprises rod-like molecules which have long-range, orientational order in one direction, but no positional order, the orientational order being about the unique, long axis. This is the phase used in the vast majority of liquid crystal displays.

All nematic phases share the feature that they are organised through a one-dimensional orientational order of molecules about their unique axis, and so it is not surprising, therefore, that there exists a nematic phase of disk-like molecules (Fig. 2b) which is, unfortunately, known commonly as the nematic discotic phase (N_D); unfortunate because phases ought to be characterised by their symmetry and not by the shape of the molecules of which they are comprised. The final example is the so-called N_{col} phase—a nematic phase of columns (Fig. 2c) which is occasionally found in the mesomorphism of disk-like mesogens.‡

Smectic mesophases

Smectic phases are layered phases which, in addition to the orientational order found in nematic mesophases, offer a degree of translational order, too. While there are several such phases, only two are described here, namely the smectic A (SmA) and smectic C (SmC) phases (note that the labels, A, C *etc.* are nothing more than labels and do not carry implicit structural information). Thus, the SmA phase is the most disordered type of smectic phase and in it, the molecules are organised perpendicular to the layer direction as indicated in Fig. 3a. In the SmC phase (Fig. 3b), the organisation is similar except that the molecules are now tilted at some angle, θ , to the layer normal; chiral versions of this phase have C_2 symmetry in the layers and as such, are ferroelectric—a property which allows their exploitation in display devices. It is important to note that in both the SmA and SmC phase, the ‘layers’ as shown in the figure are not well-defined and in fact, the organisation is best described as a sinusoidal molecular density wave. These phases

‡ Interestingly, this phase exists in both a thermotropic and lyotropic form.



Kathryn Rowe

Kathryn Rowe obtained her Ph.D. on the synthesis of metal containing liquid crystals from Sheffield University in 1997 under the supervision of Professor Duncan Bruce. She then joined Unilever Research where she became a Global Project Leader developing new antiperspirant product forms. In 2003 she joined the New Product Development group at GSK as a senior formulation scientist responsible for managing multiple projects that deliver cosmetic and OTC products to the consumer.



James Elliott

James Elliott's first job was with Omega Diagnostics in Scotland, where he was part of the team that won the Queen's export award in 1994. He graduated from Glasgow Caledonian University in 1995 and completed his Ph.D. thesis in inorganic liquid crystals at the University of Hull, under Dr John R. Chipperfield. His first postdoctoral position was with Professor Duncan Bruce at the University of Exeter, and he is currently working with Professor Ekk Sinn at the University of Missouri-Rolla in the USA.

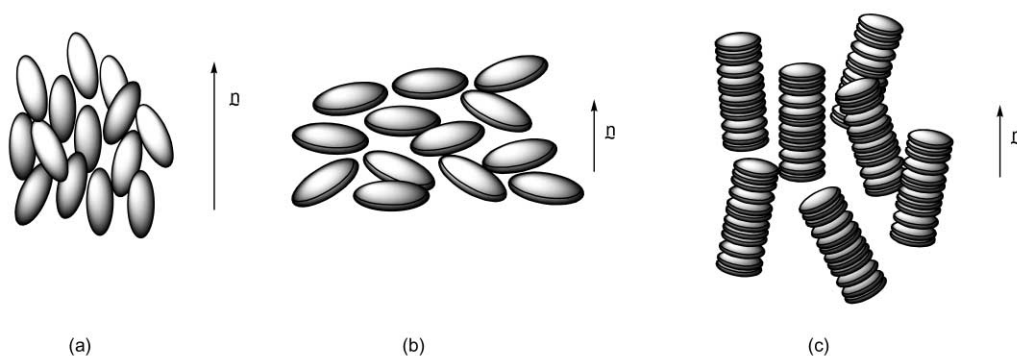


Fig. 2 Structure of three nematic phases: (a) nematic phase of rod-like molecules, N, (b) the N_D phase, (c) the N_{col} phase.

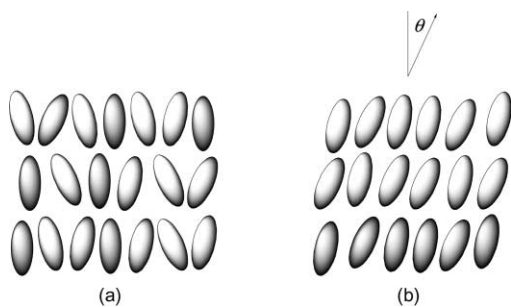


Fig. 3 Schematic structure of the SmA (a) and SmC (b) phases.

are also very fluid and there is a very high probability of molecules moving between layers.

Columnar mesophases

As the name implies, the basic building block for this type of mesophase is the column and in very many cases, the columns are formed from disk-like molecules—one reason why the

phases were commonly, but incorrectly, referred to as ‘discotic’—D, for several years. However, we now appreciate that the columns may be formed by a variety of different molecular types, and it is the arrangement of these columns in two dimensions which described the structure of the phases.

The most common types of columnar phase are the hexagonal (Col_h), the rectangular (Col_r) of which there are more than one type according to symmetry (e.g. P_{2gg} and C_{2mm}) and the oblique (Col_o). Fig. 4 shows (a-i) a side-on view of the columnar hexagonal phase and then ‘aerial’ views of the hexagonal (a-ii), oblique (b) and rectangular (c and d) lattices. In this figure, circles represent disks which are orthogonal within the columns, whereas ellipses represent disks which are tilted.

Disk-like metallomesogens forming columnar phases

The aim here is simply to design a metal complex whose shape will approximate to a disk and then surround it with a sufficient number of peripheral alkyl(oxy) chains so that a columnar

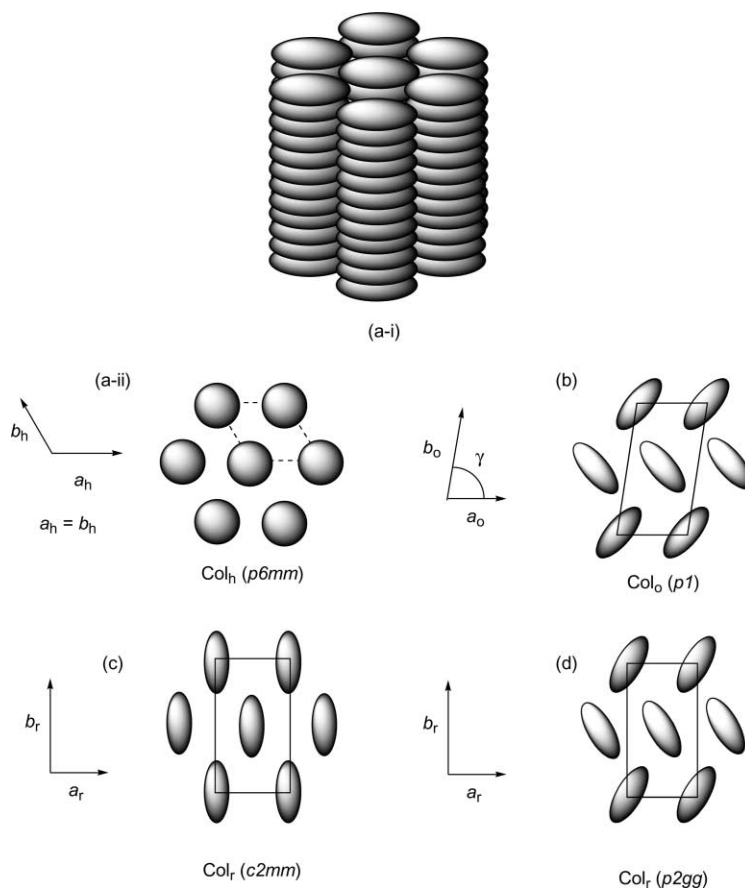


Fig. 4 Structure of the common columnar phases.

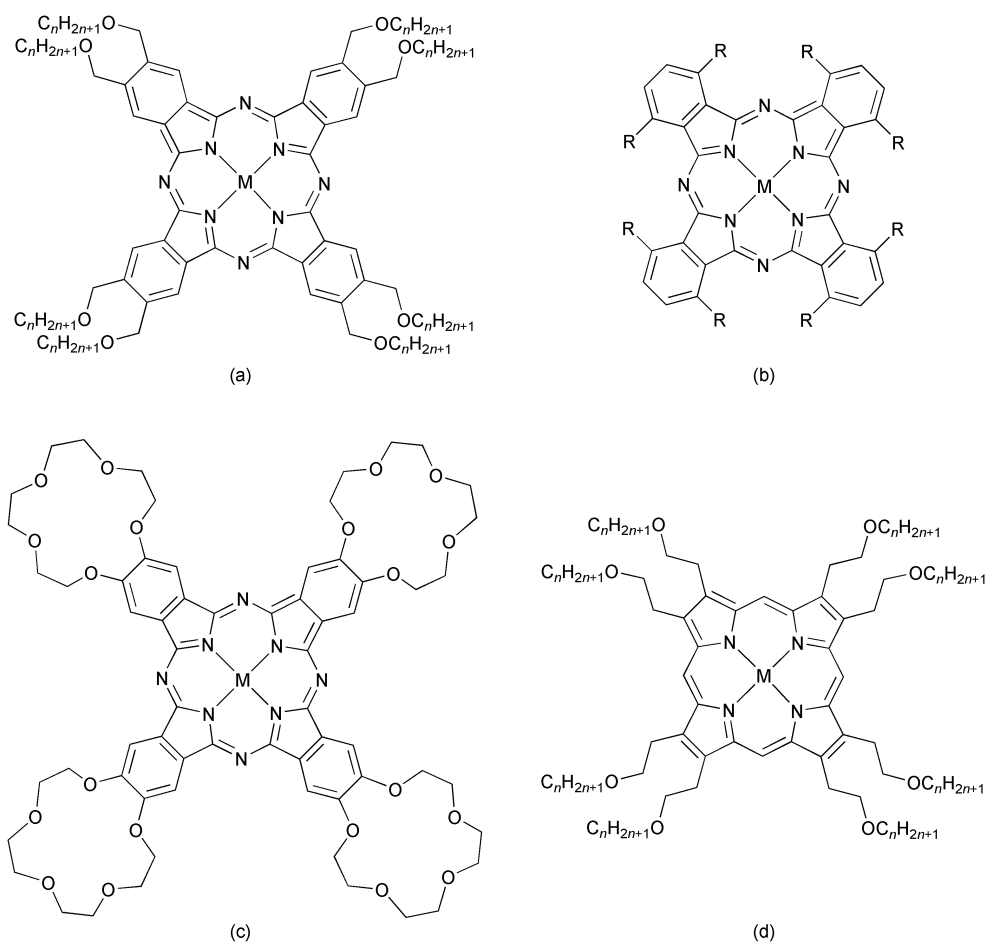


Fig. 5 Mesomorphic porphyrins and phthalocyanines.

mesophase will be stabilised. Thus, for example, there are very many examples of mesomorphic metallophthalocyanines known where the basic phthalocyanine core has been elaborated either with flexible chains (normally eight) or with more complicated organic groups which in their turn carry flexible chains. Examples are given as Fig. 5 and it should be noted that while β -substituted porphyrins (Fig. 5(d)) do form columnar phases, meso-tetraphenylporphyrins do not, forming either crystalline or 'discotic lamellar' (D_L) phases—the latter being a disordered, layer-like arrangement of disk-like molecules. This raises a design question which requires some understanding of the rôle of the peripheral chains.

Thus, the presence of the chains serves to enhance the anisotropy of the system and the fact that they are flexible and, therefore, often do not crystallise easily leads to a lowering of the otherwise high melting point of the disk core. However, the number and position of the chains is not unimportant and there is a somewhat unquantified notion that the chains should somehow properly cover the periphery of the molecule which means that with the exception of the pseudo-polymeric columnar phases of tetra(μ -alkanoato)dimetal(II) complexes (Fig. 6),⁹

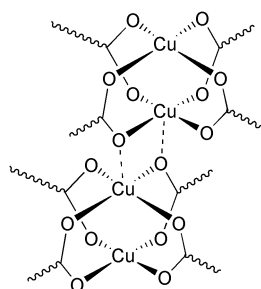


Fig. 6 Structure of the repeat unit in the mesophase of copper(II) alkanoate mesogens.

species forming columnar phases appear to require six or more peripheral chains.

This is rather well exemplified by considering a series of β -diketonato complexes of Cu(II) (Fig. 7) where the four-chained species is not mesomorphic, rather forming a crystalline lamellar phase,¹⁰ while the eight-chain complex does indeed form liquid crystal columnar phases. This is also true for

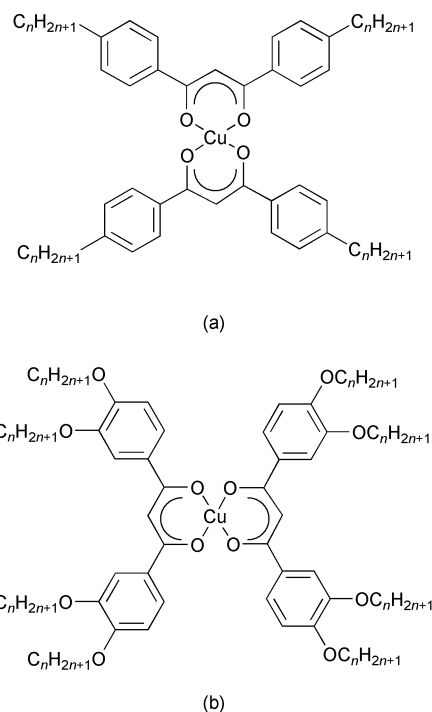


Fig. 7 Mesomorphic β -diketonates.

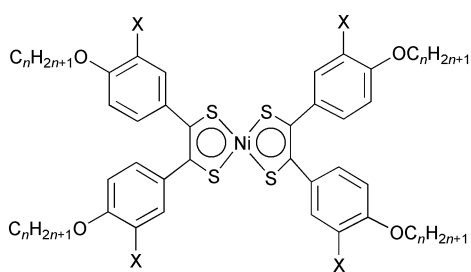


Fig. 8 Mesogenic dithiolenic mesogens.

structurally similar Ni(II) dithiolenic complexes (Fig. 8). Thus, while the four-chained derivatives (X = H) were claimed initially to show columnar mesophases,¹¹ this was shown subsequently to be a mis-assignment¹² and mesomorphic derivatives were not realised until four, further chains were added (Fig. 8, X = OC_nH_{2n+1}O).¹³

Just before leaving this small section describing β -diketonates, it is worth contemplating the two complexes shown as Fig. 9. Curiously, the more rod-like complexes (A) show columnar phases,¹⁴ while the more disk-like complexes (B) show only mesophases typical of rod-like materials!¹⁵

However, there is a subtlety to the notion of 'covering the periphery' as exemplified by derivatives of [14]aneN₄ described

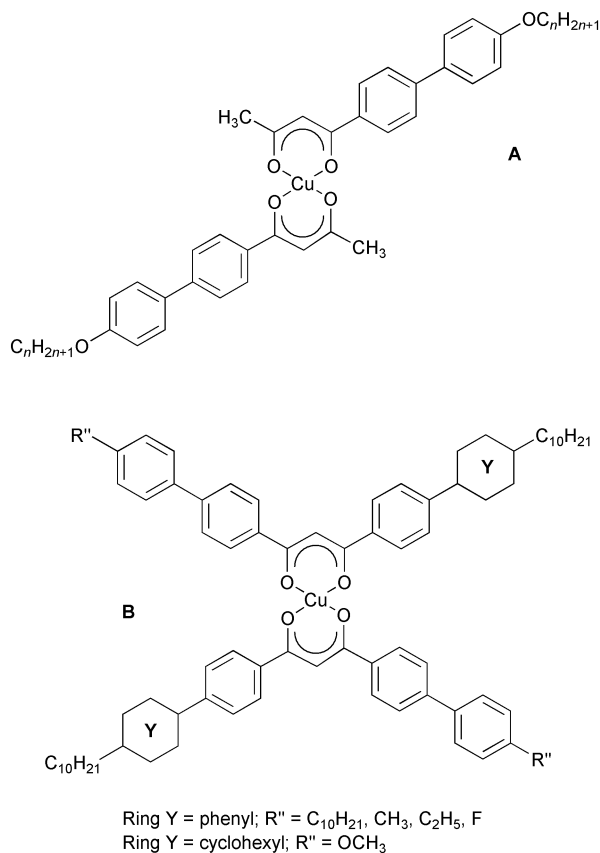


Fig. 9 Rod- and disk-like β -diketonate complexes.

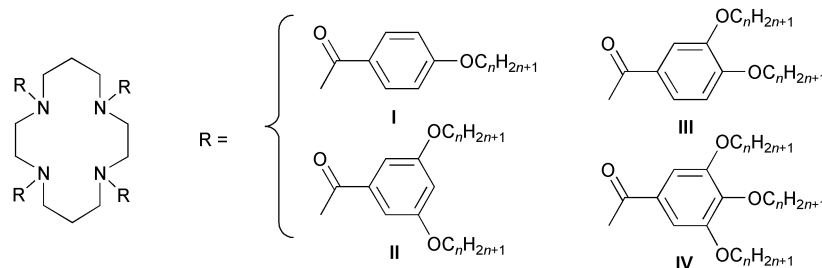


Fig. 10 Mesomorphic [14]aneN₄ compounds.

by Ringsdorf and Lattermann.¹⁶ Thus, while Ringsdorf had found that the use of 4-alkoxybenzoyl, 3,5-dialkoxybenzoyl and 3,4,5-trialkoxybenzoyl group (Fig. 10, R = I, II, IV) did not lead to mesomorphic materials, Lattermann found that the use of a 3,4-dialkoxybenzoyl group (Fig. 10, R = III) did. These materials also illustrate the fact that the central unit of a discotic mesogen does not have to be planar, and there are examples of mesomorphic hexaazacrown ethers which also testify to this.¹⁷

The interplay between ligand and metal is also a major factor in determining mesomorphism and this is illustrated with two examples. Thus, phthalocyanines have been described where the central metal moiety is a dihydroxymetal(IV) unit based on either Si or Sn.¹⁸ The materials are mesomorphic, but it is also possible to effect a polymerisation of the materials *via* a condensation reaction to realise materials which are linked spinally by -O-M-O-M- units, changing the nature of the liquid crystal behaviour from columnar to lamellar.

Another feature of phthalocyanines is, of course, the cavity size at the centre of the ring and inclusion of large metals leads to non-planar structures where the metal sits out of the plane. This is the case found in phthalocyanine derivatives of Pb(II) and the effect was to modify the arrangement in the mesophase to give an antiferroelectric arrangement (Fig. 11) which was the most efficient way for the complexes to organise and fill space.¹⁹

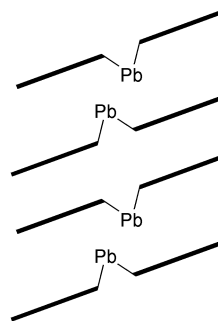


Fig. 11 Antiferroelectric arrangement of Pb(II) phthalocyanines in the mesophase.

Finally here, this discussion of discotic systems would not be complete without mention of some rather beautiful complexes in which the disk is assembled by forming multinuclear complexes. Thus, Barberá *et al.* described²⁰ some trinuclear complexes of Au(I) which formed what was described as a 'metallacrown' using disubstituted pyrazole ligands (Fig. 12). Both the complexes with X = H and X = OC₁₀H₂₁ were mesomorphic showing columnar hexagonal phases close to room temperature, although the latter complex had lower transition temperatures on account of the fact that it exists as isomers (relative orientation of the pyrazoles around the gold triangle) and that the extra chains cannot be accommodated in the molecular plane and so must reduce the structural anisotropy.

Another polynuclear system was described by Praefcke and co-workers based on *ortho*-metallated complexes of Pd(II).²¹ The formation of liquid crystals based on *ortho*-metallation is well known in calamitic systems (*vide infra*), but in these

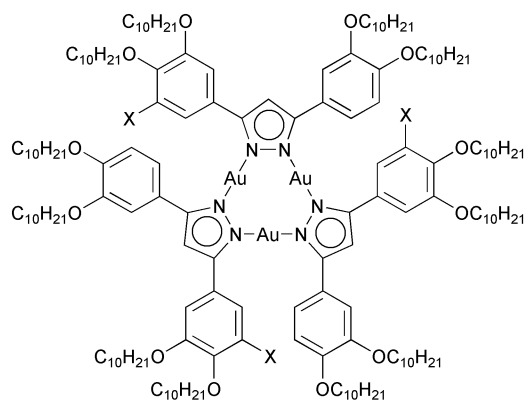


Fig. 12 Mesogens made of 'golden crowns'.

materials, the approach was cleverly extended by using larger ligands bearing two sites for *ortho*-metallation, allowing the formation of large, macrocyclic systems as shown in Fig. 13.

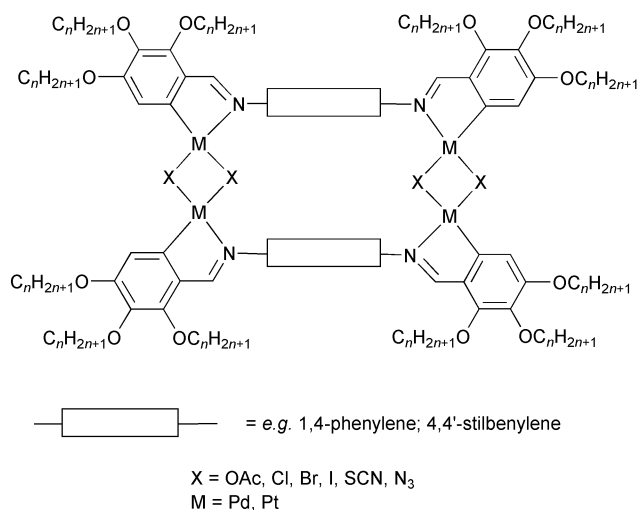


Fig. 13 Large, tetrametal macrocycles.

These complexes have a wide and varied mesomorphism. For example, thermotropically many show columnar hexagonal phases and yet in those materials which do not, it is often the case that addition of the electron acceptor trinitrofluorenone can induce a mesophase. Use of the chiral electron acceptor 2'-(2,4,5,7-tetranitro-9-fluorenylideneaminoxy)propionic acid (fortunately known as TAPA!) resulted in chiral phases. Further, in collaboration with Usol'tseva, it was found that the materials would show lyotropic mesophases in solvents such as alkanes.

Simple rod-like metallomesogens from simple rod-like ligands

In principle, the design of calamitic metallomesogens should be no more difficult than that of discotic systems given that it is known that a rod-like motif is required. However, experience shows that rod-like systems are a little more subtle, something which it is hoped will emerge from the following discussion.

Many rod-like systems have been, and continue to be, based on metals in Groups 9, 10 and 11 which are capable of forming complexes with a square-planar or linear geometry, and indeed

the dithiolenes shown in Fig. 1 illustrate this well. These complexes, along with the dithiobenzoates shown in Fig. 14,²² illustrate an important effect that complex formation can have, for while the complexes do form liquid crystal phases (and at elevated temperatures for the dithiobenzoates), the constituent ligands are not mesomorphic.

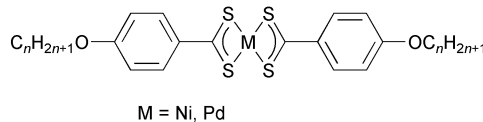


Fig. 14 Mesomorphic metal(II) dithiobenzoates.

However, this need not be the case and, for example, complexes of the cyanobiphenyl mesogens (used in commercial displays) have been complexed to Pd(II) and Pt(II) to give mesomorphic materials (Fig. 15).²³ An interesting aspect of this work was that while the ligands show only N and SmA phases, some complexes showed, in addition, a SmC phase demonstrating that coordination to form a new species can change the mesomorphism of the parent ligand.

In these complexes, there was a marked difference between the melting points (temperature at which the solid melts either to mesophase or isotropic) and the clearing points (temperature at which the liquid crystal phase becomes isotropic) when comparing Pd and Pt. This is not expected from theory and was attributed²⁴ to weaker, perhaps more labile interactions between the Pd and the organonitrile. Takahashi²⁵ later studied the directly analogous isonitrile materials for Pd and Pt with bromide and iodide ligands and found that while iodo complexes were mesomorphic for both metals, bromo complexes were mesomorphic only for Pt. However, here the melting and clearing points were *very* similar for the same combination of metal, halogen and ligand, and in these systems, the metal–ligand (isonitrile) interaction will be very much stronger than in the case of the nitriles, supporting the proposal of weak Pd–nitrile interactions in complexes of cyanobiphenyls.

There is here a curious comparison to be made between the dithiobenzoate and the cyanobiphenyl complexes, for in the former case, linking two, one-ring ligands (which are not mesomorphic) together about the metal centre leads to mesomorphic complexes and, therefore, it is not surprising that linking the mesomorphic cyanobiphenyls about a metal has a similar effect. By analogy then, one might expect that it would be possible to use, for example, 4-alkoxybenzonitriles as ligands to Pd(II) as the resulting complexes (Fig. 16) would be sufficiently anisotropic to show liquid crystal behaviour. In fact, this is not the case, yet if more chains are added to the benzonitrile (Fig. 16), disk-like materials result which show columnar phases;²⁶ related isonitriles behave similarly.²⁷

However, it is also observed that simple, linear complexes of d¹⁰ metal centres can show liquid crystal properties if acetylene ligands are used²⁸ or if complexes are formed from acetylene and isonitrile ligands (Fig. 17),²⁹ which suggests that in the simple, calamitic alkoxybenzonitrile complexes (Fig. 16), the two chloride ligands are sufficient large to reduce the anisotropy and suppress mesomorphism. This supposition finds some support in the X-ray single crystal structure³⁰ of the hexylcyanobiphenyl complex of Pt(II) (Fig. 18) which shows the steric extent of the chloride ligands.

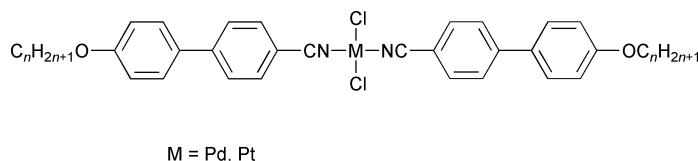


Fig. 15 M(II) complexes of cyanobiphenyls.

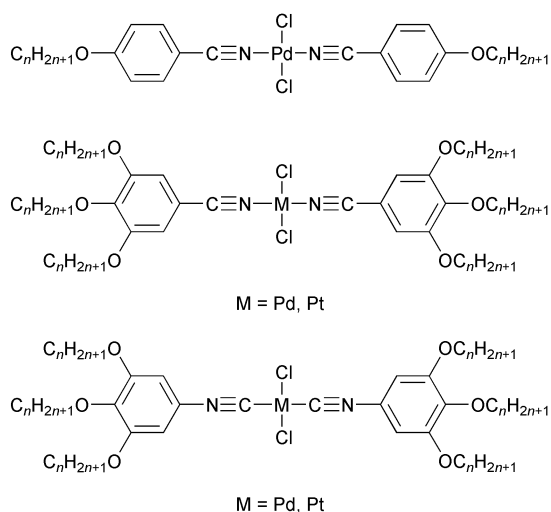


Fig. 16 Alkoxy-substituted benzonitriles and benzoisonitriles.

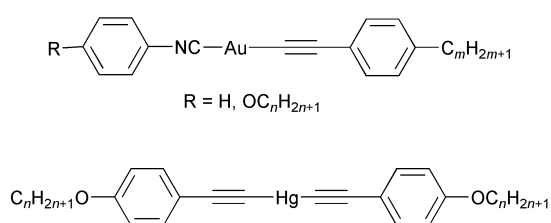


Fig. 17 Small, two-ring complexes of d¹⁰ metals.

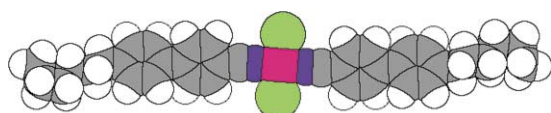


Fig. 18 Molecular structure of *trans*-[PtCl₂(NC-Ph-Ph-C₆H₁₃)₂].

Of course, other effects can come into play and there is some evidence for the action of auriphilic interactions in promoting mesomorphism in certain gold(I) and gold(III) complexes. Thus, Fig. 19 shows some gold complexes³¹ which have liquid crystal properties and which are very much 'shorter' than one might expect a compound to be to form a mesophase.

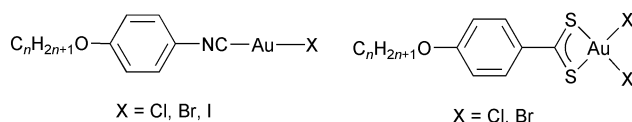


Fig. 19 Small, mesomorphic complexes of gold.

While nitriles will ligate a number of metal centres, pyridines often bind more strongly and so there was interest in their

coordination chemistry. The ligand studied most extensively is the 4-alkoxystilbazole (Fig. 20)^{32,33} and its mesomorphic complexes will be reviewed briefly. It is important to note that the ligand itself shows a crystal smectic E phase (an orthorhombic phase where rotation about the long axes is concerted within layers and where there is correlation between the layers—not a true liquid crystal phase) between around 80 to 90 °C and despite our initial reports of a SmB phase, probably no other mesophase.

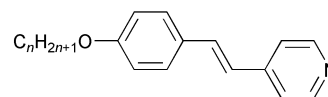


Fig. 20 4-Alkoxy-4'-stilbazole.

Pyridines can bind readily to M(II) (M = Pd, Pt) and so complexes analogous to those of the cyanobiphenyls were synthesised (Fig. 21A). The complexes of both metals melted at high temperatures ($T > 200$ °C), but for palladium, this led simply to decomposition (perhaps with transient phase formation), while for platinum, SmC phases could be observed prior to decomposition. Two strategies were then identified to reduce the transition temperatures of these materials, both of which involved employing different co-ligands. Thus, it was possible to replace the chloride ligands with alkanolate ligands (in fact, the materials were synthesised by first obtaining the desired metal(II) alkanolate and then reacting with stilbazole) which led³⁴ to complexes (Fig. 21B) in which flexible, lateral chains extended alongside the rigid core of the mesogen. In purely organic systems,³⁵ such a design invariably leads to materials which show a nematic phase as the lateral chain(s) prevent association into smectic layers and these complexes were no different showing nematic phases at temperatures of around 150 to 160 °C.

In the second strategy, the anisotropy and symmetry of the system were lowered by making an unsymmetric complex containing both a stilbazole and a coordinated alkene (Fig. 21C). These materials invariably showed a SmA phase at temperatures normally below 100 °C.^{34,36}

Monoligand complexes were also available with Rh(I) and Ir(I), and here the materials were obtained by the reaction of the ligand with [M₂(μ-Cl)₂(COD)₂] in CH₂Cl₂ under CO (Fig. 22).³⁷ The complexation had a significant effect on the ligand and now the complexes showed N and SmA phases at temperatures between around 85 to 135 °C (Fig. 23); such behaviour is typical of small, dipolar mesogens and it is clear that the *cis*-[MCl(CO)₂] unit has had a very positive effect on the mesomorphic behaviour. This is attributed to the increased linear polarisability of the complex compared to the ligand and also the enhanced anisotropy of that polarisability.³⁷⁻³⁹ Thus, for example, the linear polarisability of the ligand nearly doubles on complexation.

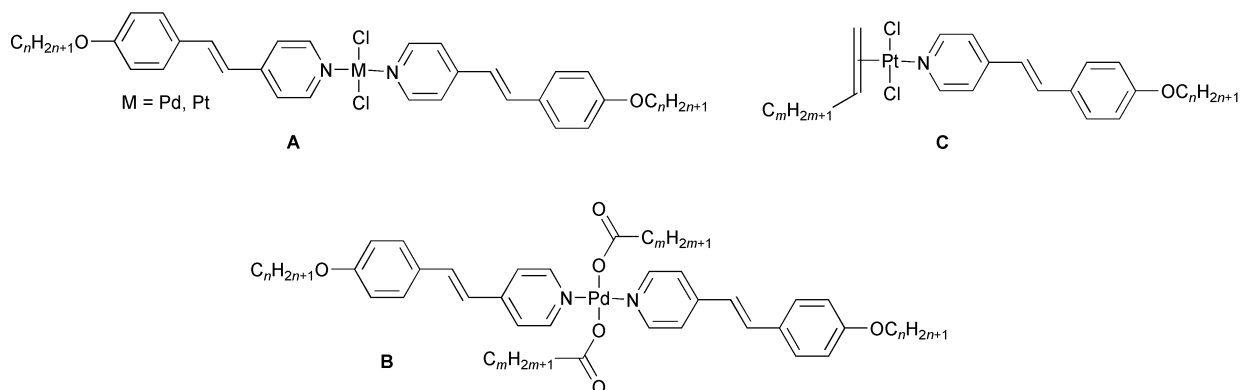


Fig. 21 Stilbazole complexes of Group 10 metals.

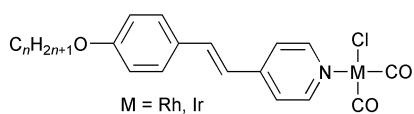


Fig. 22 Group 8 complexes of 4-alkoxystilbazoles.

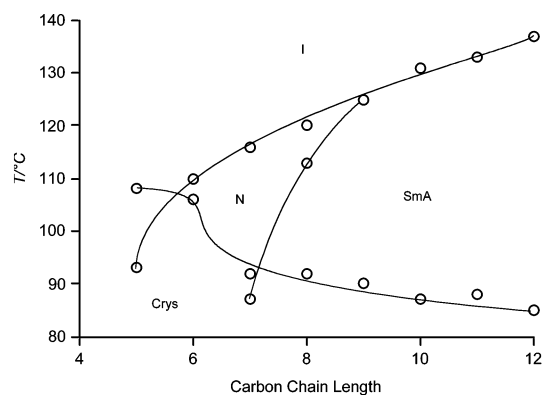


Fig. 23 Phase diagram for the Ir(I) complexes of alkoxystilbazoles.

Complexes of *ortho*-metallated ligands

In one of the earlier contributions to the study of metallo-mesogens, Ghedini and co-workers adopted a systematic approach and complexed a series of azobenzene liquid crystals to Pd(II) via *ortho*-metallation reactions, forming a series of dimeric and monomeric complexes with the general structure shown in Fig. 24.⁴⁰

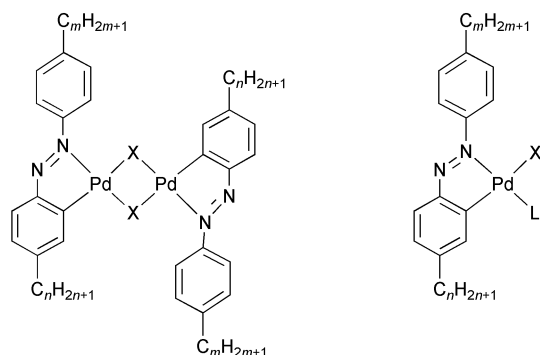


Fig. 24 *Ortho*-metallated Pd(II) complexes of azobenzene mesogens.

The dimeric complexes in particular are interesting for examination of the 'core' of the molecule suggests something disk-like, yet the distribution of chains is clearly insufficient to stabilise a columnar phase. Further, the mesomorphism is unequivocally that associated with rod-like molecules with N and SmA phases being seen and this has caused some interest in the physical properties of these materials since their initial discovery.

Such a general motif suggests scope for structural modification and some of these are described briefly now. Thus, azo compounds can be replaced by imines which can also *ortho*-metallate and, of course, monovalent, bidentate ligands can be used to cleave the dihalogen bridge to give a range of complexes, exemplified by those shown in Fig. 25.⁴¹ The complex shown as **A** showed a SmC phase and so by making the ligand chains chiral, it was possible to realise materials which showed a chiral SmC phase (labeled SmC*). As described above, such phases can exhibit ferroelectric response and ferroelectric switching was observed in the millisecond time domain. The complex shown as **B** was designed in attempts to realise a material with the biaxial nematic phase, N_b. This phase is like that shown in Fig. 2(a), but has, in addition, long-range correlations perpendicular to the main director, η . The complex possess a hydrocarbon CH₃ group and a fluorocarbon CF₃ group and it was envisaged that the incompatibility of these two

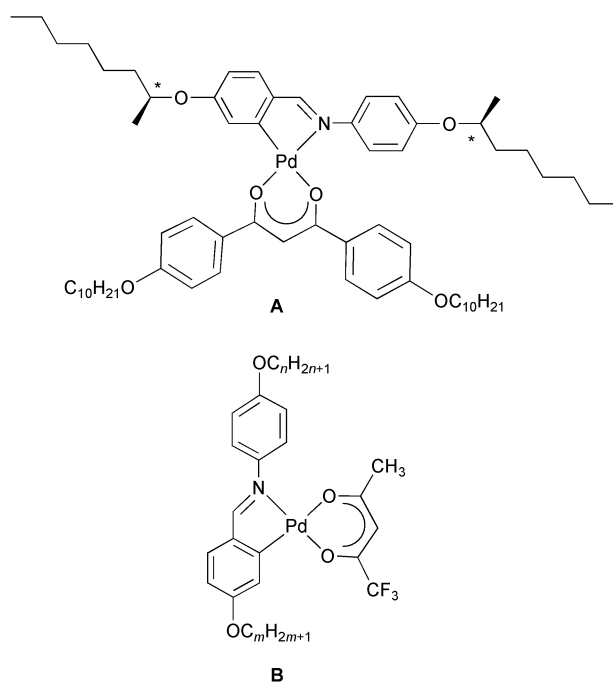


Fig. 25 Pd(II) imine complexes.

fragments might promote additional ordering. This assumption was found to be true in the solid state from a single crystal X-ray structure and ²H NMR studies in the nematic phase showed that while an N_b phase was not found, the data suggested that the design criteria adopted were valid and that the phase behaviour was not that of a 'conventional' nematic phase, but showed evidence of the behaviour predicted for the N_b phase.⁴²

Azine ligands also proved amenable to this chemistry (Fig. 26).⁴³ In the complexes where X = Cl and Br, only the *trans*

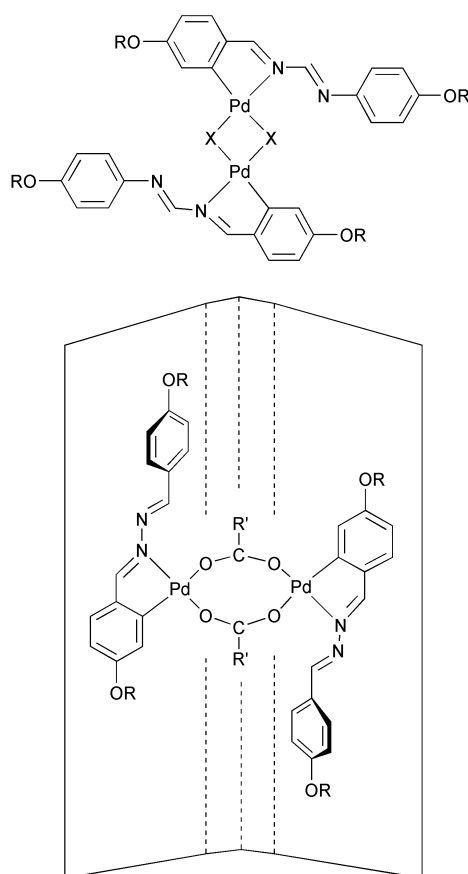
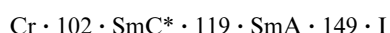


Fig. 26 *Ortho*-metallated Pd(II) azine complexes.

isomer was observed (by ^1H NMR spectroscopy), while for $\text{X} = \text{SCN}$, two isomers were observed in a 60 : 40 ratio and it was assumed that these were *cis* and *trans*. In each of these examples, the complex was assumed to be planar by comparison with related structures in the literature.⁴⁴ However, where $\text{X} = \text{OAc}$, the situation was more complex and *trans* and *cis* isomers in the ratio 3 : 1 were produced consistently. ^1H NMR studies went on to show that the *trans* isomer was optically active and hence, the structure had to be that of an 'open book' (Fig. 26, $\text{R} = \text{Me}$), although in the synthesis a racemic mixture was produced.

For the non-acetate-bridged dimers, the only mesophase seen was SmC which was typically in the range 102 to 249 °C (for $\text{R} = \text{C}_9\text{H}_{19}$) while for the acetate-bridged complexes, a nematic phase was seen for $\text{C}_6\text{H}_{13} \leq \text{R} \leq \text{C}_8\text{H}_{17}$ and for $\text{R} \geq \text{C}_7\text{H}_{15}$, a SmC phase was seen in addition. Mesophase ranges were very much larger in the planar materials.

Using the fact that the *trans*-isomer was chiral, a derivative was synthesised where the bridging carboxylate group was the optically pure (*R*)-2-chloropropionate.⁴⁵ Synthesised from the $\mu\text{-Cl}_2$ species by reaction with the sodium salt of the acid, a mixture was produced which was shown by ^1H NMR to have the following composition: *trans*- $\Delta R,R$ (34%), *trans*- $\Delta R,R$ (34%), *cis*- R,R (32%). Thus, while the *trans*-components described a pair of diastereoisomers, the *cis* isomer was optically pure by virtue of the chiral acid groups. The mixture so produced had the phase sequence:



and physical measurements showed that the SmC* phase was ferroelectric, with a rise time of around 330 ms at a square wave voltage of ± 17 V and 0.5 Hz and a cell thickness of 11 μm . Such response times were some three orders of magnitude longer than those found in SmC* phases of more conventional, calamitic, organic materials, something probably due to the greater viscosity of the palladium complexes which in turn resulted from the molecular shape.

Complexes of *ortho*-metallated ligands and of salicylaldimines

If, arguably, the cation $[\text{Ru}(\text{bipy})_3]^{2+}$ is the drosophila fly of coordination chemistry (at least in terms of photochemistry), then metal complexes of salicylaldimines perform a similar function in the study of metallomesogens. The first reports of mesomorphic derivatives were made by Galyametdinov who was followed by Ghedini, Serrano, Hoshino and then many others. A generic structure is shown as Fig. 27 and the literature up to about 1998 is well described in a review by Hoshino.⁴⁶

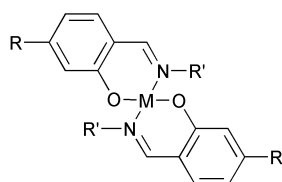


Fig. 27 Basic structure of metal complexes of salicylaldimines.

The beauty and attractiveness of these systems is that they are readily and widely variable and that they can form stable complexes with a range of metals. For example, Ni, Cu, V=O, Fe-Cl and Pd have all been incorporated and, more recently, work by Galyametdinov⁴⁷ followed by ourselves⁴⁸ and then Binnemans,⁴⁹ has shown that they can act as ligands to the full range of lanthanide elements. A range of representative structures for these materials is given in Fig. 28,^{46,50,51} and certain Pd(II) derivatives have recently been shown to have good photorefractive properties.⁵²

Table 1 Thermal behaviour of metal salicylaldimine complexes (2)

M	$n = m$	Transition	$T/^\circ\text{C}$	$\Delta H/\text{kJ mol}^{-1}$
Pd	10	Cr-Col _h	99	128
		Col _h -I	104	5.6
Pd	16	Cr-Col _h	52	134
		Col _h -I	111	3.6
Cu	10	Cr-I	93	^b
Cu	16	Cr-Col _h	57	135
		Col _h -I	102	4.5
Ni	10	Cr-I	77	^b
Ni	16	Cr-I	90	^b
Fe-Cl	10	Cr-Col _h	68	^b
		Col _h -I	172	15
Fe-Cl	16	Col _h -I ⁺	160	16

^a Melting point not seen as the material is obtained as a glass and forms a glass on cooling. ^b Measurement not possible due to compound cooling into glassy state.

It is not proposed to discuss the rod-like derivatives in any detail, but one or two points are pertinent. First is that in considering the structures of some derivatives, particularly those with *N*-aryl groups, the position is similar to that found in the basic *ortho*-metallated palladium complexes as the 'molecular core' is almost disk-like, yet the phases shown are typically N, SmA and SmC. Second is the observation that these ligands gave the first examples of calamitic, paramagnetic materials through the work of Galyametdinov, and several EPR studies have subsequently been carried out. Third is that derivatives showing columnar phases⁵³ appear effectively non-existent, save for two isolated reports (Fig. 29).⁵⁴

However, examination of these ligands shows that they are readily functionalised as the 'synthetic deconstruction' in Fig. 30 illustrates. Therefore, we undertook the synthesis of some more heavily substituted derivatives in order to realise columnar phases, details of which are presented in Scheme 1.

The material targeted used a combination of 4-alkoxybenzoate functions attached to the aniline ring and 3,4,5-trialkoxymethylbenzoate functions attached to the salicylaldehyde ring. In the scheme, the reduction of the nitrobenzene to the aniline may also be accomplished using hydrogen over Pd/C, or using hydrazine over Pd/C. Complexation of the ligands was achieved by reaction with the metal acetate ($\text{M} = \text{Pd}, \text{Cu}, \text{Ni}$) or chloride (Fe). All new materials were obtained pure as evidenced by CHN analysis and ^1H and ^{13}C NMR spectroscopy (except for those containing paramagnetic metal centres).

For all ligands synthesised (1), the chain lengths of the two parts of the molecule were the same ($n = m$) and it was found that none of the ligands was mesomorphic, melting to the isotropic state at temperatures between 58 °C ($n = m = 16$) and 168 °C ($n = m = 1$). In considering the metal complexes (2), chain length was clearly a major factor in destabilising the crystal phase to reveal the liquid crystal phases, for none of the complexes with $n = m = 1$ or 4 was mesomorphic and melting points were between ca. 160 and 290 °C. It was only at much longer chain lengths that any mesophases were seen and, then, not for each metal. The thermal behaviour of derivatives with $n = m = 10$ and 16 is summarised in Table 1.

All of the mesomorphic complexes showed a columnar hexagonal phase which was readily identified by its optical texture (Fig. 31). In comparing the behaviour of the different complexes, several points are worthy of further consideration. Thus, none of the Ni(II) complexes was mesomorphic but the very broad nature of the NMR spectra indicated that they were paramagnetic and hence, did not exist in a planar geometry. The most likely alternative would be tetrahedral or some twisted state on the way from square planar to tetrahedral,

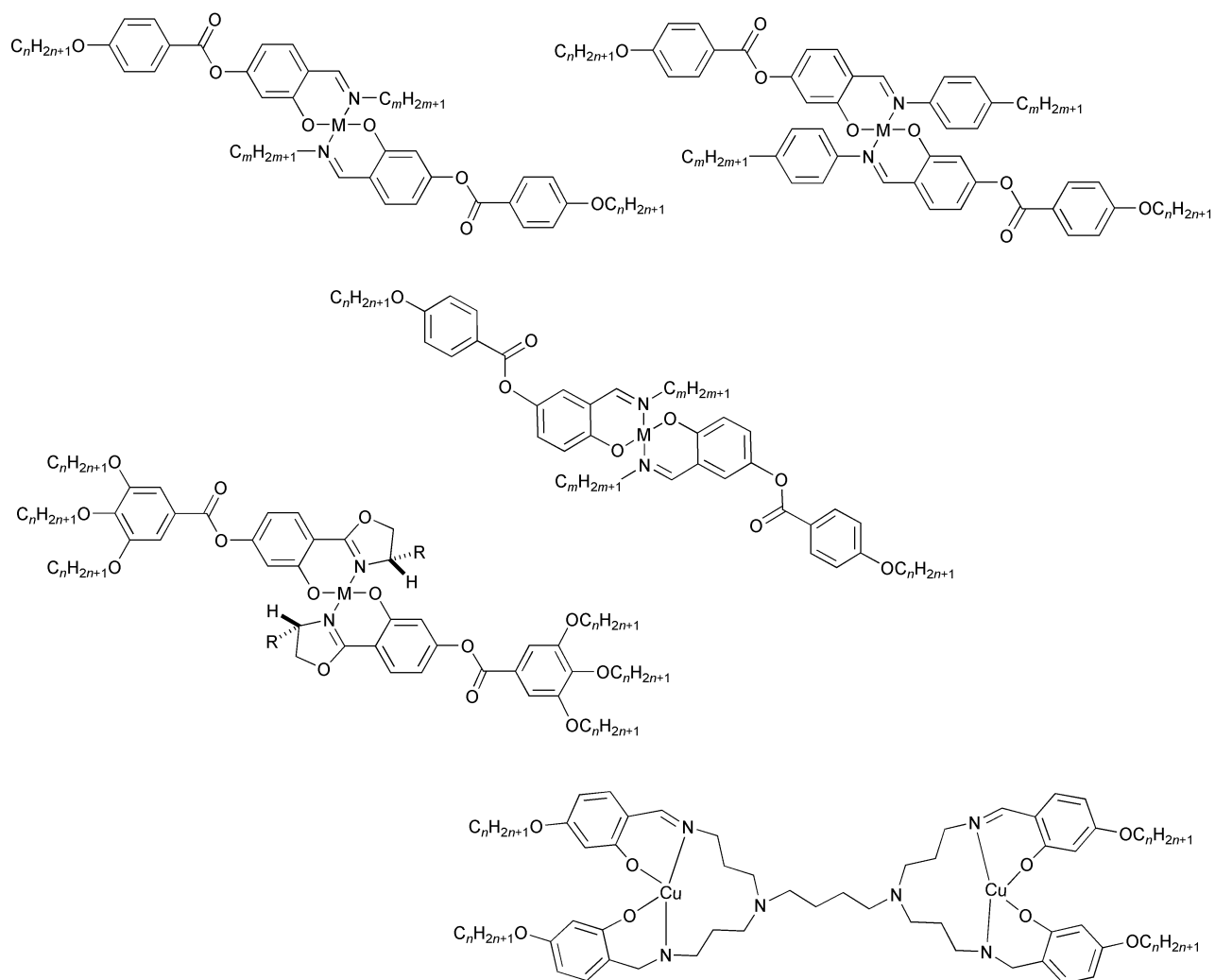


Fig. 28 Illustrative metal salicylaldimine complexes.

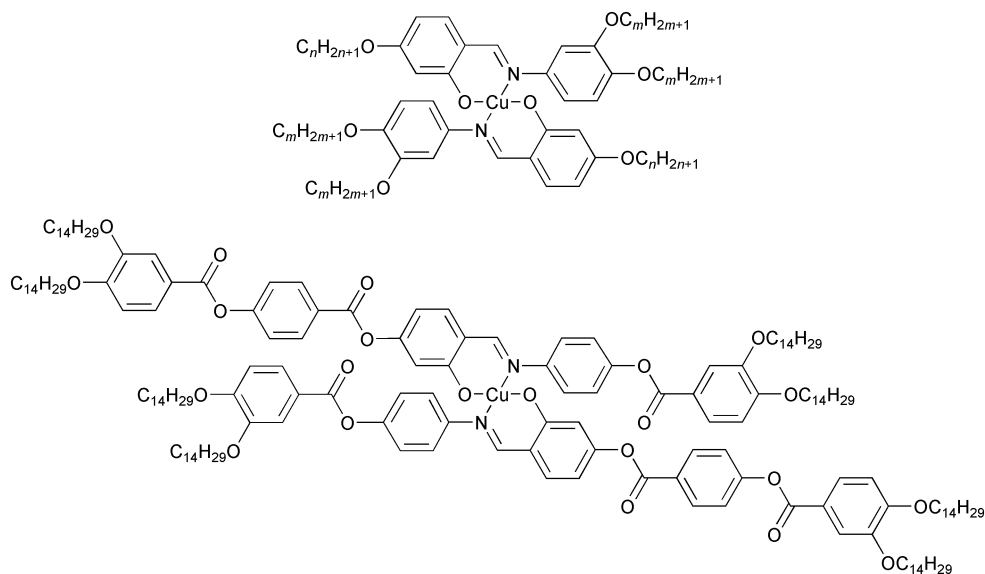


Fig. 29 Salicylaldimine complexes showing columnar phases.

leading to bulky structures with little or no anisotropy, suppressing totally liquid crystal phase formation. This is consistent with the observed melting points which are lower than might have been expected by comparison with, for example, the clearing points of the Cu(II) complexes (for related materials where one is mesomorphic and the other not, it is appropriate to compare the melting point of the non-mesomorphic derivative with the clearing point of its mesomorphic counterpart).

That only one copper complex is mesomorphic is not so easy to explain as the thermal properties are similar to those of the palladium complexes, suggesting that the decyloxy derivative might have been expected to be mesomorphic.

The palladium complexes were square planar (good NMR spectra were obtained) and here, both complexes showed a columnar hexagonal phase. Interestingly, lengthening the chain from decyloxy to hexadecyloxy significantly destabilised the

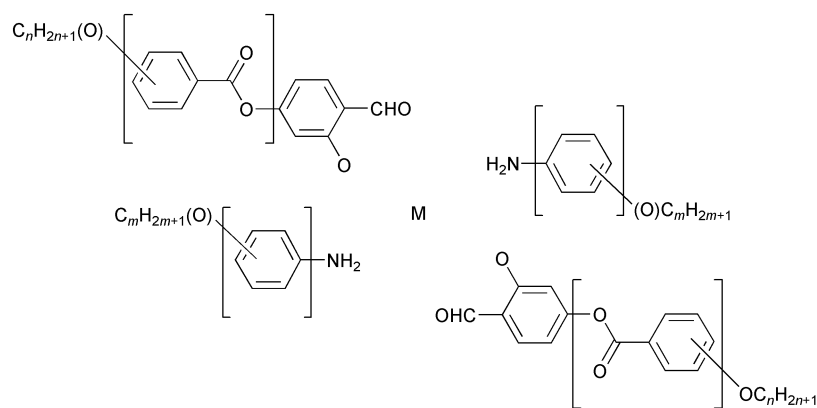
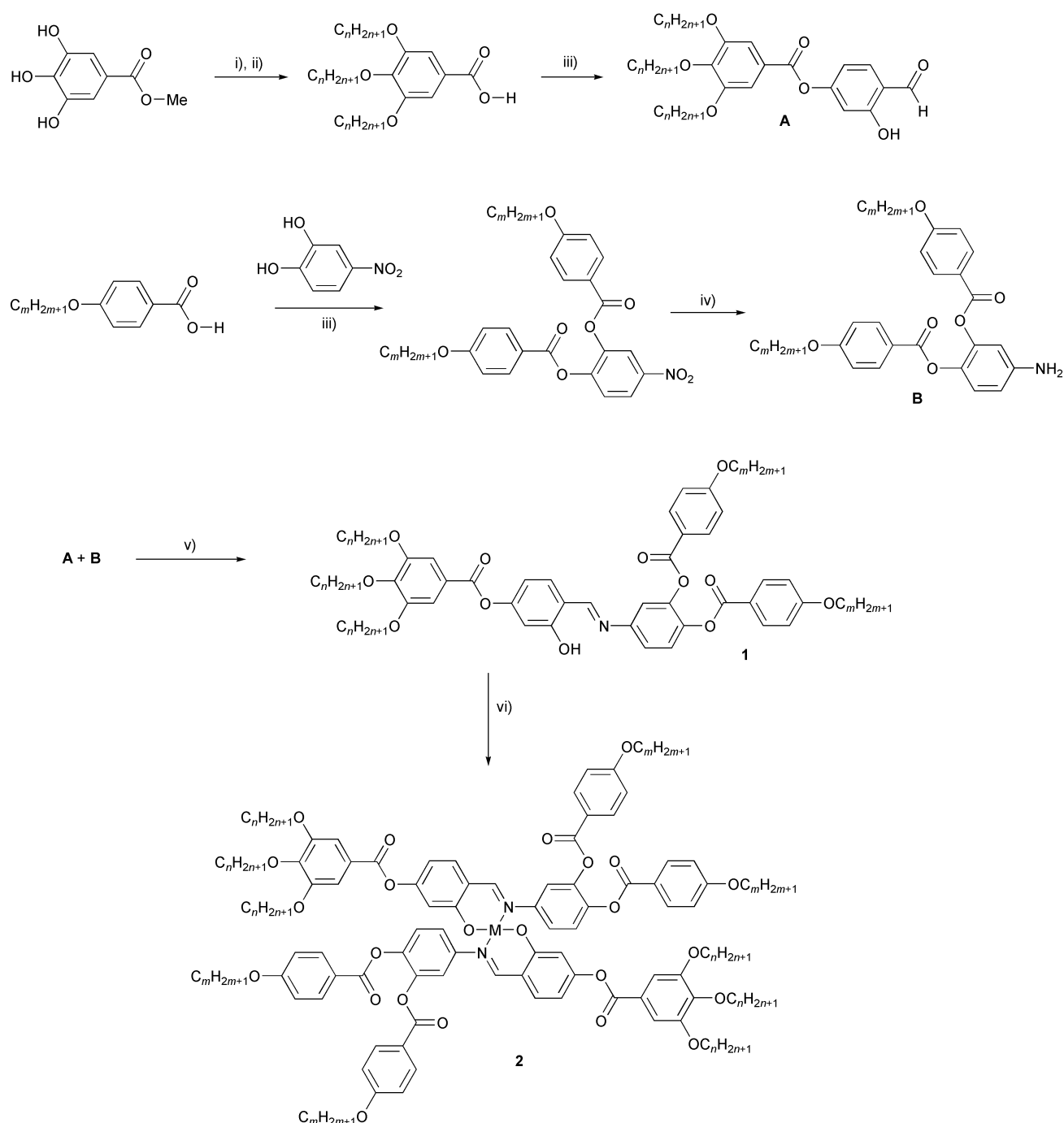


Fig. 30 'Synthetic deconstruction' of mesomorphic metal salicylaldimate complexes.



Scheme 1 Synthesis of the salicylaldimine ligands. i) $C_nH_{2n+1}Br/K_2CO_3/DMF/\Delta$; ii) $KOH/EtOH/\Delta$; iii) $DCC/DMAP/molecular\ sieves/THF$; iv) $SnCl_2 \cdot 2H_2O/PrOH/\Delta$; v) $EtOH/H^+(cat.)/\Delta$; vi) $[M(OAc)_2]$ ($M = Pd, Cu, Ni$) or $FeCl_3/PrOH/\Delta$.

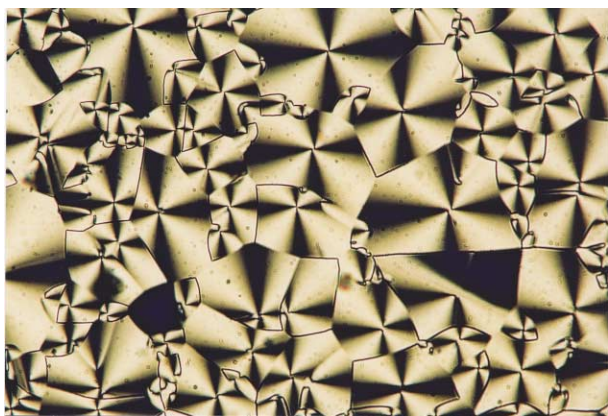


Fig. 31 Optical texture of the columnar hexagonal phase of **2** (M = Pd).

crystal phase (as it did with the copper derivatives), yet stabilised the mesophase. Finally here, we note that the chloroiron(III) complexes show the most stable mesophases of all, with the Col_h phase clearing above 150 °C. Of course, these complexes are not planar, rather being based on a square pyramidal geometry. As such, the complexes might be considered as 'bowlic' in nature, implying a stacking as indicated in Fig. 32 which would provide additional sterically driven interactions between the molecules, further stabilising their organisational state. Such arrangements have been proposed before in calixarene complexes of W(VI)⁵⁵ and in oxovanadium(IV) mesogens,⁵⁶ for example.

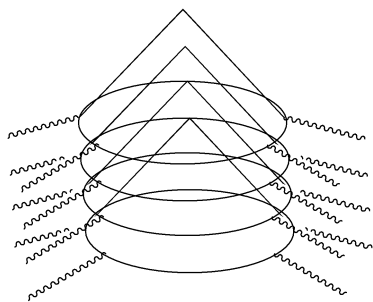


Fig. 32 Schematic drawing of the packing in bowlic mesogens.

Thus, with a versatile ligand base, it is possible to realise a variety of complexes not only from the point of view of including several metals, but also in terms of the chemical modification which is possible allowing properties to be tuned from rods to disks.

In contemplating the mesomorphism of the Fe(III) complexes above, we might begin to consider how, if at all, high coordin-

ation number metal centres might be incorporated into liquid crystals while retaining the structural anisotropy necessary for mesophase formation. In order to pursue this discussion, it is necessary to introduce one more aspect of liquid crystal behaviour, namely the mesomorphism of polycatenar liquid crystals.

Polycatenar liquid crystals

Polycatenar mesogens^{54b,57} are based on a calamitic motif (Fig. 33), having a rather extended, central core which terminates in several alkoxy chains, hence giving rise to the name polycatenar (literally many-tailed). The nomenclature of polycatenar systems depends on the number of terminal chains, so that those with four chains are termed *tetracatenar*, those with six chains *hexacatenar* and so on.

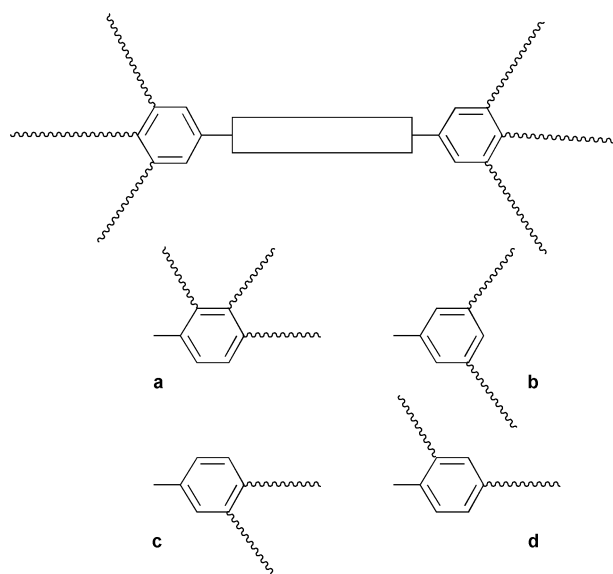


Fig. 33 Schematic representation of polycatenar mesogens showing different potential terminal ring configurations.

The number and arrangement of the chains has a profound effect on the mesomorphism and emphasis will be given here to tetracatenar mesogens in which the terminal chains are in the 3,4-positions of the terminal rings.

For pentacatenar and hexacatenar mesogens, the dominant phase is columnar and this mesomorphism arises as the extended and numerous terminal chains occupy a very large volume, preventing the molecules existing within a lamellar phase as they would be unable to fill the space (Fig. 34).

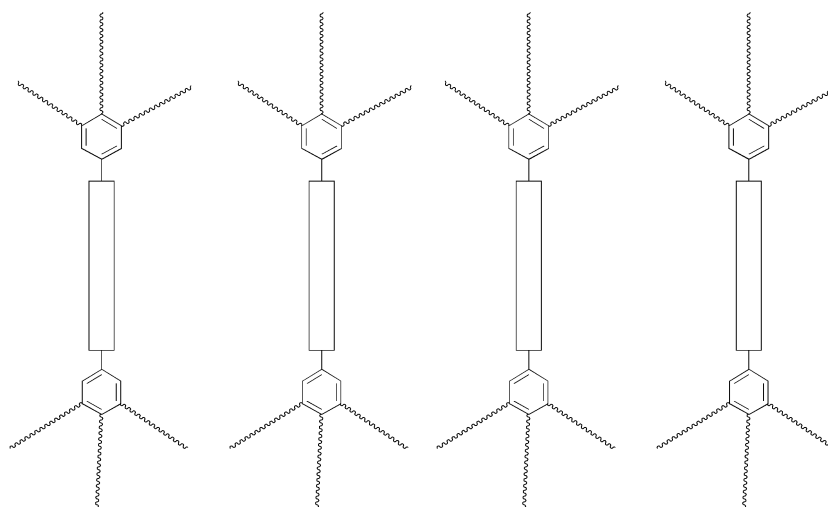


Fig. 34 'Cartoon' to show the poor space-filling ability of hexacatenar mesogens.

However, experimental observations are consistent with the idea that perhaps three of these molecules might come together to describe a circular cross-section (Fig. 35), many of which could stack up to give columns which would organise into a mesophase. The orientation of the molecules from one 'slice' of column to the next is random.

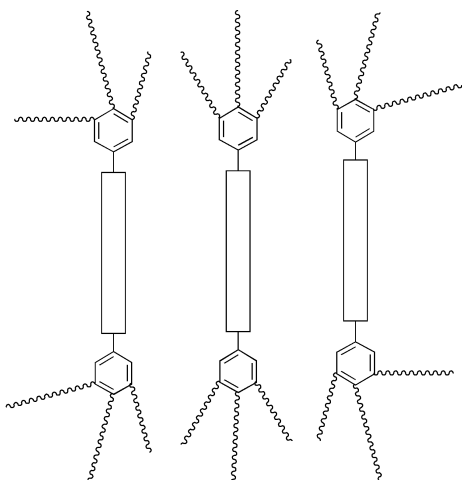


Fig. 35 Schematic representation of hexacatenar mesogens in the columnar phase.

The reason for the interest in the tetracatenar systems mentioned is that short-chain-length homologues show nematic and/or SmC phases, while longer-chain homologues show columnar phases—that is to say the mesomorphism of rods and disks can be combined into a single, homologous series. Thus, when the chain length is short, the materials resemble calamitic materials and so N or smectic phases are expected. However, as the chains lengthen or as the temperature increases, the volume the chains occupy increases and so, as for the hexacatenar systems above, they cannot organise into lamellar phases and so columnar phases result. The nature of this transition is discussed elsewhere.⁵⁸

High coordination number systems—interplay between metal and ligand

Calamitic systems

This discussion commences in considering the palladium-imine complexes described above and here, *ortho*-metallation was used to generate metallomesogens in which the metal was formally high-coordinate due to the inclusion of a Cp ring (Fig. 36).^{59,60}

Ortho-metallation is also known for Mn(I) and Re(I) and imine ligands were employed to make mesomorphic complexes of the octahedral, d⁶ ions; representative structures are shown in Fig. 37.^{61,62}

One thing which characterises both the Pd–Cp complexes and these metal tetracarbonyls is that the ligand systems are somewhat more extended than the other *ortho*-metallated systems described, and groups that reported the high-coordination-number systems observed that for smaller, two-ring ligands, mesomorphic complexes did not result. The reason for this lies in the structural anisotropy required to ensure

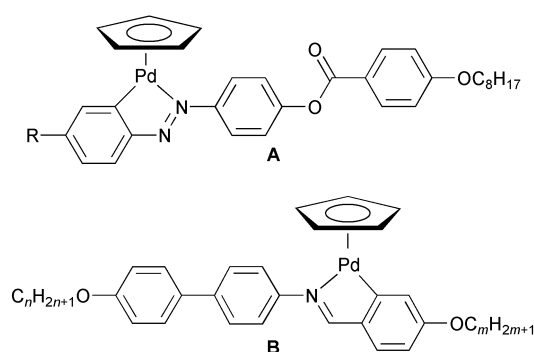


Fig. 36 High-coordinate Pd–Cp complexes.

mesophase formation, for the introduction of the ligand(s) which increase the coordination number (Cp for Pd and two CO ligands for Mn/Re) reduces this anisotropy greatly. The only way that the effect of this reduction can be overcome is to make the ligands more anisotropic so that these ligands have a proportionately smaller, negative effect.⁶³

Another important point in relation to all these materials is that they show only nematic phases and this bears comment. Perhaps the fullest comparison^{62a} is for the Re(I) complexes with four rings in the ligand (Fig. 37A; M = Re) where the mesomorphism was determined for a large number of ligands as both *n* and *m* were varied. Typically the ligands showed the following phase sequence: §

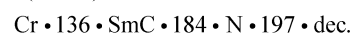


in the overall range of about 90 to 300 °C, whereas all of the complexes showed only the nematic phase and normally in the range 120 to 180 °C. The suppression of the smectic phases (in these and the ligands of the Pd complexes) and the reduction in transition temperatures reflect the introduction of a group which perturbs the anisotropy of the system. Thus, mesophase stability in less anisotropic systems is reduced and the fact that the perturbation is located as a kind of lateral group prevents smectic phase formation, leaving the nematic as the only one seen.

In order to see how general such arguments might be, it is necessary to consider a small collection of high-coordination-number systems and these are now discussed. From our own work with the Mn(I) and Re(I) imines, we were keen to establish whether the use of more extended ligands would amount to a general approach to realising mesomorphic complexes where the metal was six coordinate. Thus, a series of 1,4-diazabutadiene complexes was synthesised and then complexed to Re(I) as shown in Fig. 38.⁶⁴

The mesomorphism of ligand and complex are exemplified in the following example:

Ligand **3** (*n* = 10)



Complex **4** (*n* = 10)

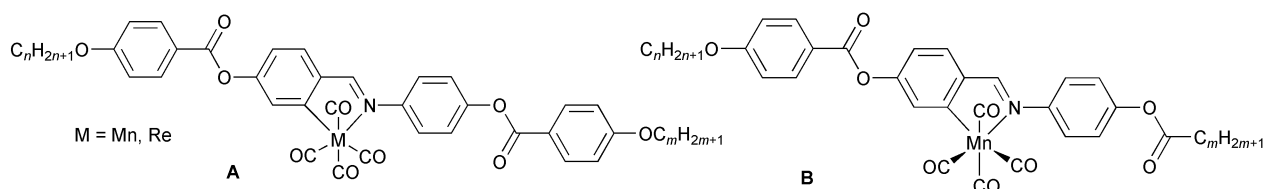


Fig. 37 Mesomorphic Group 6 imine complexes.

§ The J phase is a crystal smectic rather than a true smectic phase. The SmI phase is a fluid, tilted hexagonal phase.

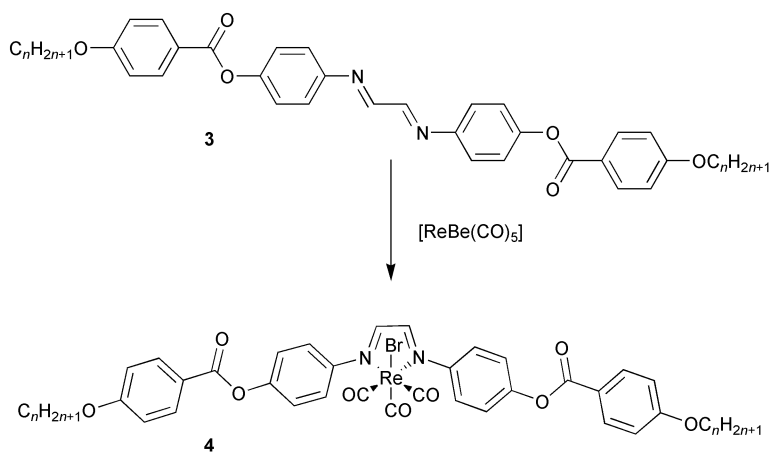


Fig. 38 Mesomorphic Re(I) diazabutadienes.

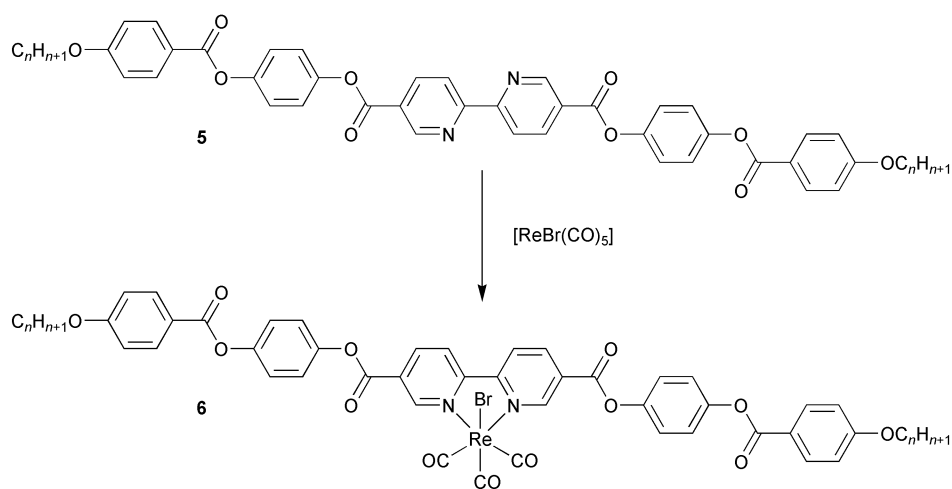


Fig. 39 Mesomorphic Re(I) complexes of 2,2'-bipyridines.

Thus, the transition temperatures are not reduced on complexation and, indeed, in some longer-chain homologues, it was observed that the SmC phase of the ligand was retained on complexation.

Next, we can consider another family of α -diimines and their complexes, this time based on 5,5'-disubstituted-2,2'-bipyridines (Fig. 39).^{63a}

Here, the mesomorphism is exemplified by the following example:

Ligand **5** ($n = 12$)

Cr • 210 • M • 212 • SmC • 328 • N • 341 • dec.

Complex **6** ($n = 12$)

Cr • 238 • SmC • 267 • N • 296 • I

Here, there is some reduction in transition temperatures, but no loss of the smectic phase upon complexation.

What the above results show is that in the two α -diimine systems, there is no major reduction in transition temperatures as was found with the Re(I) imines, and that the smectic phases found in the ligands can be retained in the complexes. The difference in the diimine systems is that, as indicated in the respective figures, the free ligands exist in a *transoid* arrangement which becomes *cisoid* on complexation. Thus, from a ligand with no dipole moment associated with the diimine function, a complex is generated where an appreciable dipole moment exists (e.g. calculated gas-phase dipole moment for 2,2'-bipyridine is 3.7 D) and there is, in addition, an appreciable dipole moment associated with the Re–Br bond. By contrast, in the imine systems, there is no conformational change on complexation

and no strongly polar function associated with the ligated 'Re(CO)₄' unit.

Therefore, we sought some other systems which might act as comparators in order that we might delineate the effect of the ligand conformational change and any dipoles associated with the metal fragment. In making this comparison, we turned to tetracatenar complexes of a series of diimine complexes which are now described.

Polycatenar systems

In addition to the simple, calamitic bipyridines described above, the synthesis was undertaken of some tetra- and hexa-catenar derivatives, too.⁶⁵ Of these, it is the tetracatenar derivatives (Fig. 40) which are of interest here (ligands are compound **7**), and their complexes (**8**) with Re(I).

The thermal behaviour of the ligands has been reported in detail⁶³ and, typically for tetracatenar materials, they show N and SmC phases at short chain length and Col_h phases at long chain length; certain intermediate chain lengths also show a cubic phase, although a discussion of the nature of this fascinating, 3-D phase is beyond the scope of this manuscript. These ligands may then be reacted with [ReBr(CO)₅] to give bromorheniumtricarbonyl complexes (**8**) and a comparison of the mesomorphism for certain ligands and complexes is given in Fig. 41 (labeling on the *x*-axis corresponds to the compound number with the carbon chain length in parentheses).

What is found is that the clearing point of the complexes is reduced over that of the ligands, although while there is a gentle decrease in the clearing point of the ligands, it increases steadily in the complexes. The ligands show only Col_h phases for the homologues under consideration and while the complexes also

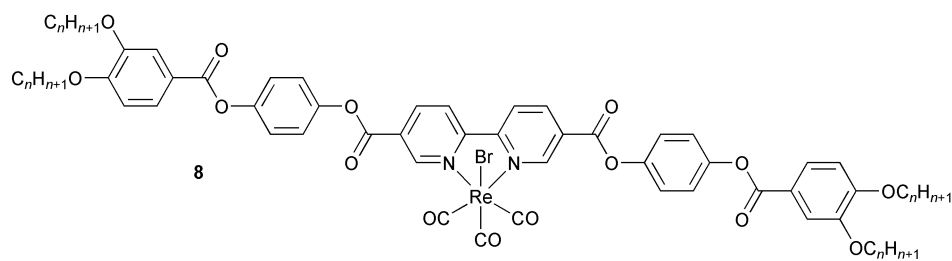


Fig. 40 Tetracatenar bipyridine complexes of Re(I).

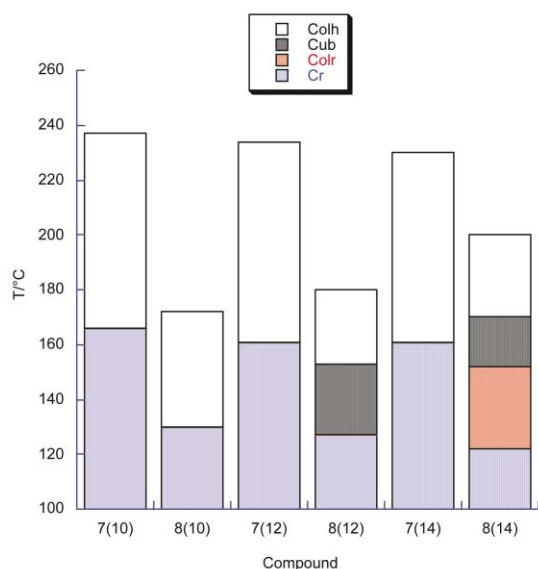


Fig. 41 Comparative mesomorphism of bipyridine ligands **7** and their Re(I) complexes **8**.

show this phase, the two longer-chain homologues both show a cubic phase (symmetry $Ia\bar{3}d$);⁶⁶ the longest-chain homologue shows a Col_r phase in addition, although its symmetry has not been determined.

In order to take the change in ligand dipole into account, we then proceeded to synthesise some tetracatenar 3,8-disubstituted phenanthrolines (Fig. 42) as a permanent dipole moment of 4.1 D⁶⁷ exists due to the fixing of the ring nitrogens by the exocyclic double bond.

These ligands are not direct analogues of the bipyridines as the 'arms' are bound to the core by acetylene functions rather than esters, but nevertheless are comparable in most other ways. Once more, the ligands (**9**) show N and SmC phases at shorter chain lengths and the Col_h phase for longer-chain homologues and a curious feature of these compounds is that the change from SmC to Col_h mesomorphism happens with the addition of

a single methylene unit to the terminal chains, so that the dodecyloxy homologue shows *only* a SmC phase while the tridecyloxy homologues shows *only* a Col_h phase. This is rather unexpected and this progression from lamellar to columnar phases in tetracatenar mesogens has been discussed elsewhere.^{58b,68} The mesomorphism of the ligands (**9**) and their Re(I) complexes (**10**) is then compared in Fig. 43.

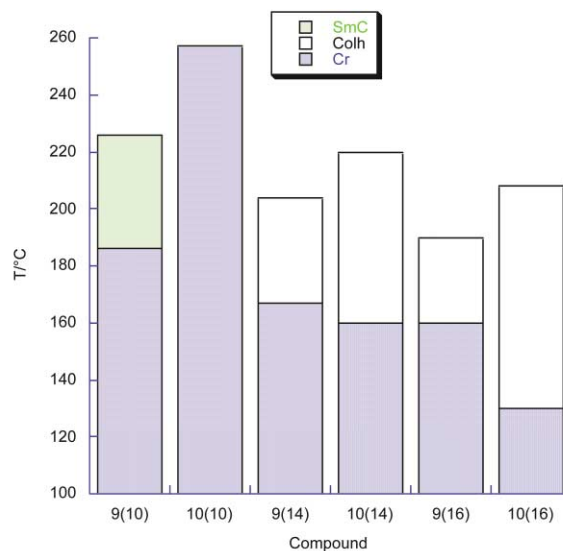


Fig. 43 Comparative mesomorphism of the phenanthroline ligands **9** and their Re(I) complexes **10**.

The first thing that the plot shows is that the clearing points decrease in both ligand and complex with increasing chain length, in contrast to the behaviour of the bipyridines. The ligand and decyloxy homologue shows a SmC phase which disappears on complexation, but the tetradecyloxy and hexadecyloxy homologues show the Col_h phase in both ligand and complex. However here, the clearing point of the complexes is higher than that of the ligands and the mesomorphic range is wider in the complexes due to some destabilisation of the crystal phase.

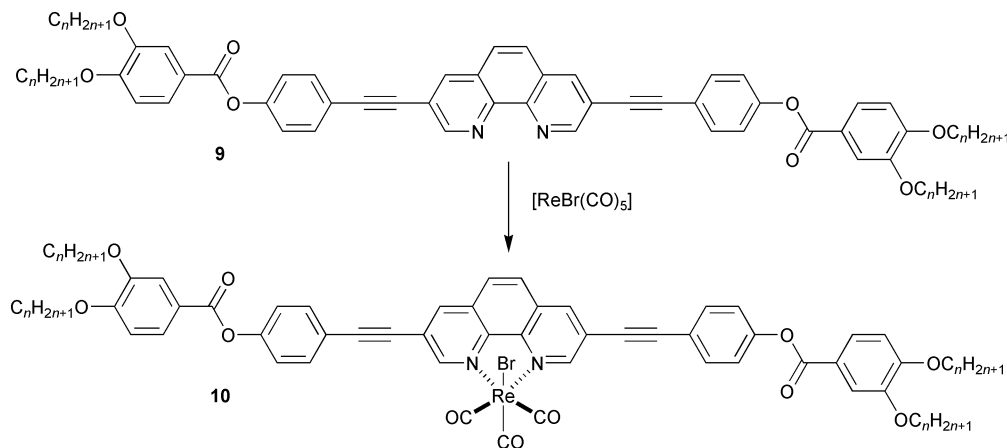
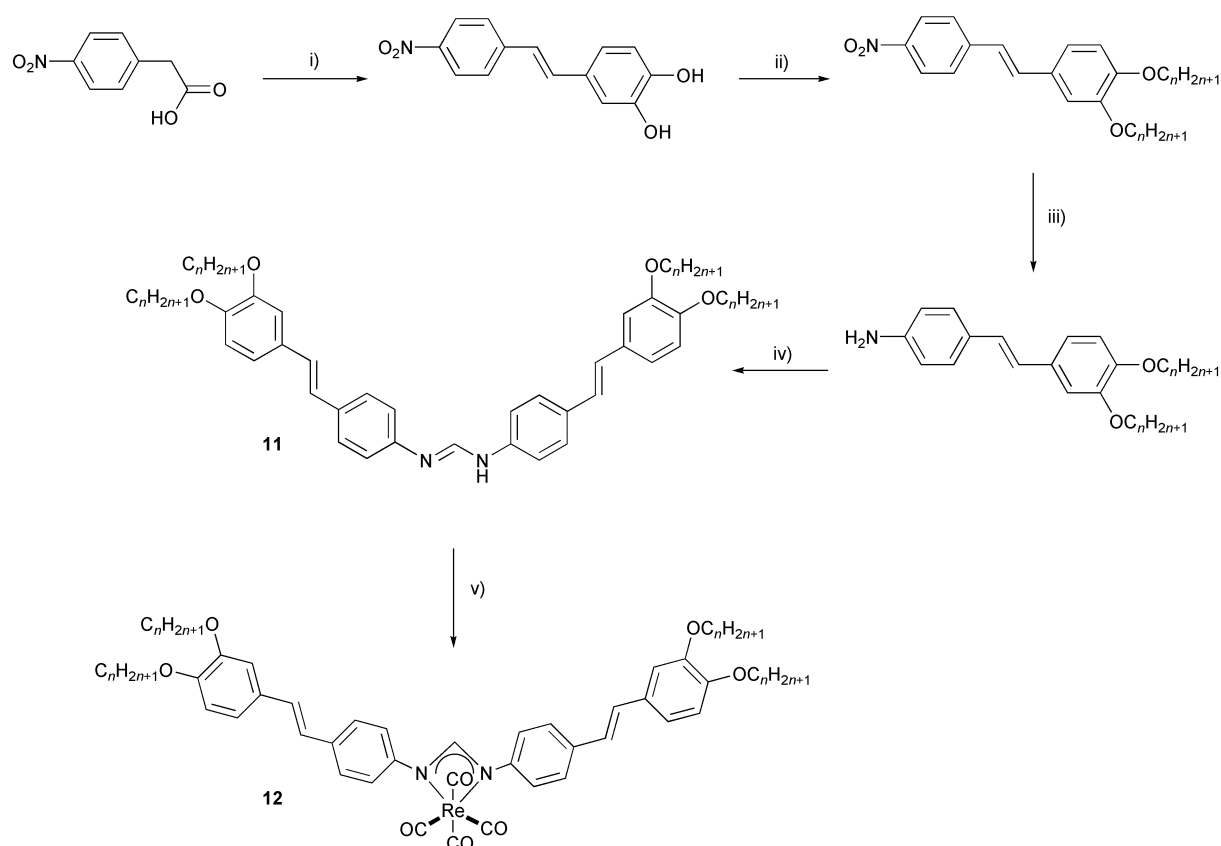


Fig. 42 Tetracatenar phenanthrolines and their Re(I) complexes.



Scheme 2 Synthesis of the mesomorphic amidines (**11**) and their complexes of Re(I) (**12**): i) 3,4-dihydroxybenzaldehyde/piperidine/butanol/ Δ ; ii) $C_nH_{2n+1}Br$ /butanone/NaI/ Δ ; iii) hydrazine/Pd/C/EtOH; iv) triethylorthoformate/toluene/AcOH/ Δ ; v) $[ReMe(CO)_3]$ /toluene/ Δ .

Thus, there is a very different pattern of behaviour in the phenanthroline materials.

The final class of ligands and complexes to be considered are based on an amidine function which has never previously been employed in liquid crystal compounds to the best of our knowledge. The structure of the ligands and their complexes is shown in Scheme 2. These ligands were chosen for, while they possess a permanent dipole moment as drawn in the scheme, the 'Re(CO)₄' group does not contribute a significant dipole on complexation in contrast to the 'ReBr(CO)₃' unit.

The ligands themselves (**11**) were indeed mesomorphic and formed columnar phases over a relatively narrow range of temperature, not far above 100 °C. These ligands are quite different from the bipyridine and phenanthroline materials as they bend at the amidine carbon and, it is assumed, adopt the motif suggested in the scheme. On complexation, it is assumed that the ligand opens out a little, but that the complexes are still bent about the Re centre. The mesomorphism of ligand (**11**) and complex (**12**) are presented in Fig. 44, plotted on the same scale as those discussed previously for ease of reference.

In this series, fewer comparisons are available but nevertheless, trends are apparent. Thus for both ligand and complex, clearing point and melting point decrease with increasing terminal chain length and this time it is noted that the transition temperatures and mesomorphic range in the complexes are appreciably lower than in the free ligands.

Conclusions

So what might be learned from the three series of materials above? The results from the amidines are consistent with those discussed earlier with regard to calamitic imines in which the 'Re(CO)₄' unit acted to reduce transition temperatures, although the effect is not so great. With the bipyridine systems, complexation (this time of an 'ReBr(CO)₃' group) once more

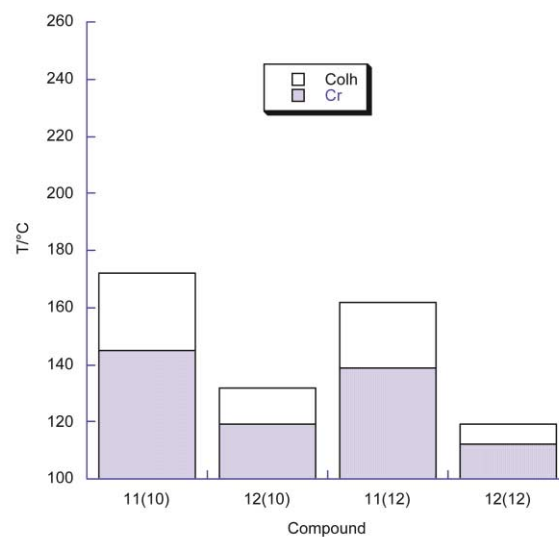


Fig. 44 Comparative mesomorphism of the amidine ligands **11** and their Re(I) complexes **12**.

led to a reduction in transition temperatures, although in the complexes themselves, these transition temperatures increased with chain length, contrary to observations made for the amidines. However, the phenanthrolines were different again and in these systems, the clearing point of the complexes were higher than those of the ligands.

There is clearly no obvious set of factors which will explain the above behaviour consistently, yet there are lessons apparent in controlling both transition temperatures and, to a degree, mesomorphism. It is clear that all of these properties are a complex and delicate function of the chemical composition of the system and that surprises await those who would seek them.

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