

## Dalton Perspectives

# The Synthesis and Properties of Metal-containing Liquid-crystal Systems: What can the Metal do for You?

Duncan W. Bruce

Centre for Molecular Materials, Department of Chemistry, The University, Sheffield S3 7HF, UK

In this perspective, some of the general phenomena associated with liquid-crystal behaviour are introduced before selective consideration is given to the effect which a metal can have when it forms part of a liquid-crystalline molecule.

The field of metal-containing liquid crystals is now growing quite fast and it is not intended here to give a review-style overview of the whole area—interested readers are referred to four recent reviews.<sup>1</sup> In this article, it is intended to pick out specific examples from both our own work and that of others to try to illustrate the effect that inclusion of a metal atom can have on the properties of liquid-crystal systems. The article is structured to give a brief introduction to liquid crystals for the first-time reader. It then goes on to discuss the choice of complex to be elaborated in order to generate a liquid-crystalline material, and then to discuss the properties which may be introduced.

### Liquid Crystals

In considering the liquid-crystal state, it is important to realise that it represents a discrete state of matter, lying between the solid and liquid states, and therefore possessing properties characteristic of each. Thus, for example, liquid crystals are fluid like liquids, but also have partial translational and/or orientational order, reminiscent of solids. The consequences of having both fluidity *and* order means that the fluids are anisotropic; this property has led to both academic interest and to applications.

Liquid-crystal phases (mesophases) may be classified on the basis of the shape of the molecules which give rise to the phase [*i.e.* are the molecules rod-like (calamitic) or disc-like (discotic)?], the method of inducing the mesophase [action of temperature (thermotropic) or of solvent (lyotropic)], and whether we are dealing with low- or high-molar mass (polymer) systems. For the purposes of this article, only low molar mass, thermotropic systems of the calamitic and discotic types will be discussed.

*The Structure of Mesophases.*—In considering the structure of mesophases, we will regard our molecules as either featureless rods or discs. If such rods were to arrange themselves in a way that they were in a fluid state, with one-dimensional orientational order and no positional order, then they would describe a nematic phase (N) (Fig. 1). The orientational order in the phase is an averaged order and the degree of correlation, known as the order parameter ( $S$ ), between the average direction (defined by the director,  $n$ ) and the actual orientational directions of all the molecules is given by the function (1), where  $\theta$  is the angle between the long molecular

$$S = \frac{1}{2} \langle 3 \cos^2 \theta - 1 \rangle \quad (1)$$

axis and the director. Typically,  $0.4 < S < 0.7$  for a nematic phase. The nematic phase is the most disordered type of mesophase and is the one used in most display applications.

If we then introduce partial positional order in addition to the orientational order, a family of smectic phases can be generated, which are characterised by having some layering of the molecules. For example, in the smectic A ( $S_A$ ) phase [Fig. 2(a)] the molecules are loosely associated within layers and, on average, all point in a direction perpendicular to the layer normal. The situation in the smectic C phase ( $S_C$ ) is similar [Fig. 2(b)], except that the director now makes some angle,  $\theta$ , to the layer normal. There is however no positional correlation between molecules within the  $S_A$  or  $S_C$  layers and indeed, in each case, there is considerable fluidity within, and easy diffusion between, the layers.

Another group of smectic phases is generated by introducing

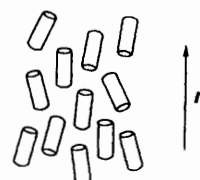


Fig. 1 Schematic diagram of a nematic phase

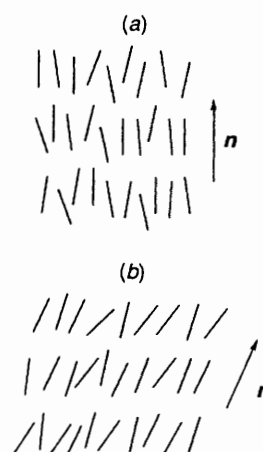


Fig. 2 Schematic representation of the  $S_A$  (a) and  $S_C$  (b) phases

some symmetry into the layers. Thus the  $S_B$  phase has the molecules arranged in a hexagonal fashion within the layers with a director perpendicular to the layer normal (Fig. 3). The  $S_F$  and  $S_I$  phases (Fig. 3) are tilted variations of this phase, with the tilt lying across a hexagonal edge or along a hexagonal vertex, respectively (the labels attached to all these smectic phases are purely historic in origin and convey no other information). Chiral variants of the  $N$ ,  $S_C$ ,  $S_F$  and  $S_I$  phases have long been known and such variants of the  $S_A$  phase have more recently been described.<sup>2</sup> These will not be discussed further here.

We can also consider the formation of discotic phases by discs and in such cases it is the correlation of the unique, short molecular axis which is in question (Fig. 4). Thus, it is possible to have a discotic nematic phase,  $N_D$ , in which there is orientational correlation of the short molecular axis in the absence of any positional ordering (Fig. 5).

In addition, there is a whole family of columnar phases in which the molecules are stacked in columns which are then arranged with respect to one another. These phases are distinguished as ordered ( $D_o$ ) or disordered ( $D_d$ ), according to the absence or presence respectively of liquid-like order within the columns. A further classification describes the packing of the columns with respect to one another. Two examples would be hexagonal ( $D_{ho}$  or  $D_{hd}$ ) and rectangular ( $D_{ro}$  or  $D_{rd}$ ) (Fig. 6).

**Molecular Considerations.**—It is now appropriate to put some chemical flesh on our featureless rod and disc. A typical

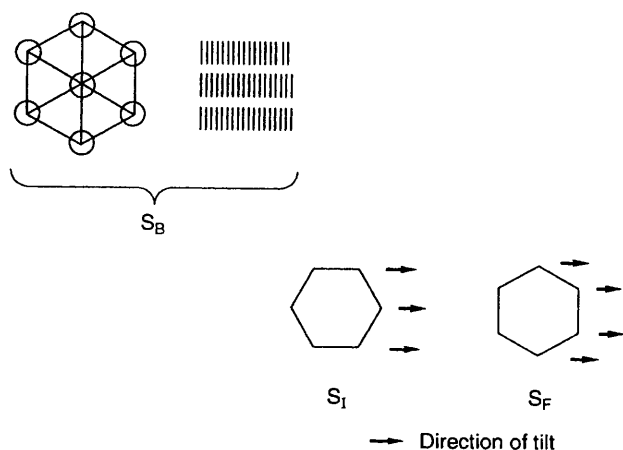


Fig. 3 Schematic diagram showing the structure of some hexagonal smectic phases

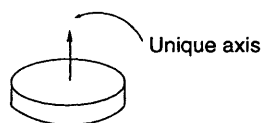


Fig. 4 Schematic representation of the molecular structure of discotic materials



Fig. 5 Schematic representation of the nematic discotic phase

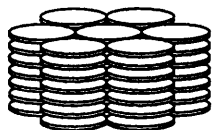


Fig. 6 Schematic of a  $D_{ho}$  phase

schematic diagram describing the features necessary in a calamitic (rod-like) molecule is shown in Fig. 7. While this is discussed in detail elsewhere,<sup>3</sup> it is important to point out that a crucial feature is the structural anisotropy of the molecules, giving rise to an anisotropy of electronic polarisability which generates the weak, anisotropic dispersion forces which stabilise the liquid-crystal phases. Aside from that, it is sufficient here to point out that the 'ring' is most usually phenyl (although heterocycles and cyclohexyl are common) and the terminal groups A and B are often both alkyl or alkoxy chains, although the combination of a chain and a polar group is common. The linking group, X, can take several forms (e.g.  $\sigma$  bonds;  $-N=N-$ ,  $-\text{CO}_2-$ ,  $-\text{CH}=\text{CH}-$  or  $-\text{CH}_2-\text{CH}_2-$ ) but almost always preserves the overall linearity of the molecule (i.e.  $-\text{O}-$  would not be tolerated in most cases) and, where aromatic groups are involved, the conjugation is often preserved too. Selected examples are given in Fig. 8.\* In the case of discotics, the rules are effectively much less rigorous and appear in general terms to require some sort of flat core (e.g. azacrown, phthalocyanine or polyaromatic), surrounded (usually) by six or more peripheral chains. This is illustrated in Fig. 9.



Fig. 7 A generalised structure for calamitic, liquid-crystalline molecules

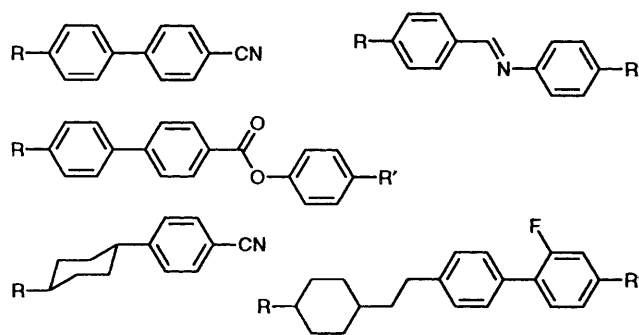


Fig. 8 A few examples of organic, calamitic liquid crystals

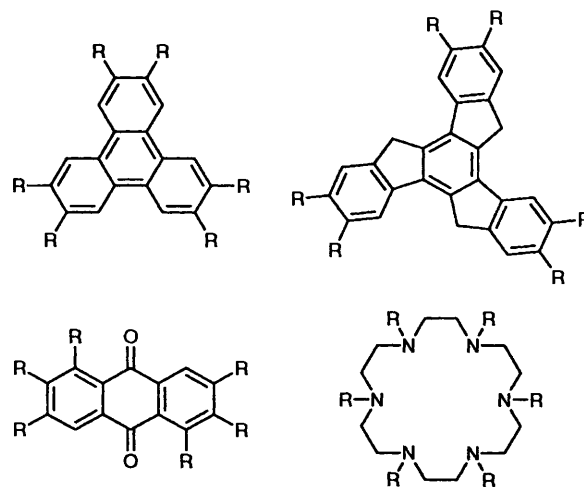


Fig. 9 Some examples of discotic materials

\* Here and elsewhere, R, R' designate long chain substituents, usually simple alkyl or alkoxy functions.

Despite all of these general rules, many groups are sailing, synthetically speaking, into new waters, and readers are referred to two excellent reviews which give an overview of shapes and strategies.<sup>4</sup>

### How to Choose a Potential Metal Complex System

However it may first look, metal-containing liquid crystals are not simply obtained by adding long alkyl chains onto your favourite molecule—at least not usually! The right materials are generated by a slightly more careful consideration of how the design criteria above might be applied. Interested readers are referred to ref. 1(b) which gives a fairly comprehensive listing of the structural types of metal complex which have so far given rise to liquid-crystal systems.

**Discotics.**—The area of discotics is perhaps the easiest and it is relatively obvious that a whole family of phthalocyanines will form discotic mesophases. This is in fact the case and the idea has been well exploited, in particular by Simon.<sup>5</sup> Many different metals have been incorporated and highly anisotropic semi-conducting systems and antiferroelectrically stacked systems have been demonstrated.<sup>1,5</sup> Other macrocyclic systems also suggest themselves as candidates for study and several examples have been reported over the last few years, notably by Lattermann *et al.*<sup>6</sup> and Lehn *et al.*<sup>7</sup> The effect of the metal in determining the mesomorphism of macrocyclic materials is nicely demonstrated by the work of Gregg, Fox and Bard<sup>8</sup> who synthesised a series of octaethanol porphyrins (Fig. 10; R = CH<sub>2</sub>CH<sub>2</sub>OC<sub>n</sub>H<sub>2n+1</sub>).

Most of the free-base porphyrins show no mesophase whatsoever, but on the introduction of one of several metals (*e.g.* M = Zn, Cu or Cd), a discotic phase is stabilised. Cook *et al.*<sup>9</sup> also found that the mesophase stability in a series of phthalocyanines was metal dependent and that zinc stabilised the mesophase more effectively than either nickel or copper.

Use can also be made of the central metal in these systems and spinally linked, polymeric systems (Fig. 11) have been reported.<sup>10</sup>

**Calamitics.**—In choosing candidate systems for the synthesis of calamitic metal-containing materials, a little more care ought

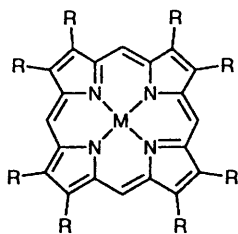


Fig. 10 Mesomorphic octaethanol porphyrin derivatives

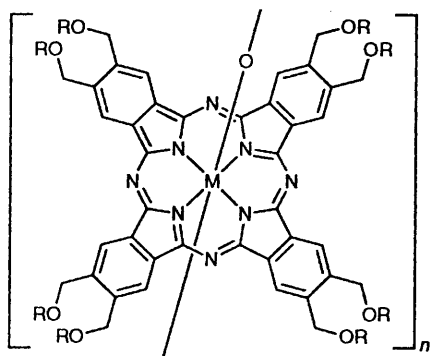


Fig. 11 Spinally linked, polymeric phthalocyanines

to be exercised. It is certainly the author's view that with a reasonable amount of background knowledge and experience, complexes which will be mesomorphic can be properly designed, but the author is more than willing to acknowledge that luck (or serendipity, to use the IUPAC name) is a valuable co-worker. Thus, in designing the mesomorphic dithiolenes complexes of Ni and Pt (Fig. 12), Giroud-Godquin and Mueller-Westerhoff had argued that the two M-S-C-C-S rings would act together as equivalent to a phenyl ring and so produce analogues of terphenyl.<sup>11</sup> Although it subsequently turned out that the terphenyl analogy was incorrect, the general basis underlying the assumption was good, and materials with nematic and smectic C phases resulted.

Broadly speaking, most of the known calamitic metal-containing systems have three things in common. First, they contain a metal in a d<sup>8</sup>-d<sup>10</sup> configuration, secondly, they contain a mesogenic ligand (mesogenic is used here in the broadest sense of being 'liquid-crystal-like,' rather than specifically implying that the ligand actually has liquid-crystal properties) and thirdly, the ligands are either actually or effectively *trans* disposed about the metal. Suitable examples would therefore be the palladium(II) and platinum(II) complexes of cyanobiphenyls<sup>12</sup> [Fig. 13(a); d<sup>8</sup> metal, liquid-crystalline ligands], platinum(II) complexes of acetylides<sup>13</sup> [Fig. 13(b); d<sup>8</sup>

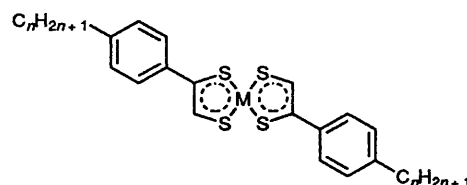


Fig. 12 Dithiolenes complexes of Giroud-Godquin and Mueller-Westerhoff

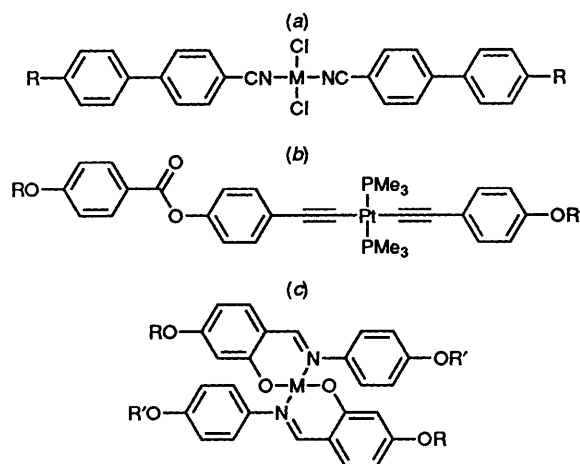


Fig. 13 Examples of some calamitic metal-containing liquid crystal systems

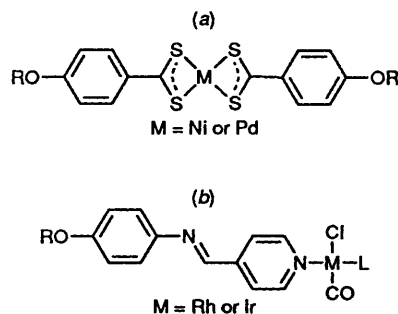


Fig. 14 Mesomorphic metal complexes derived from non-mesomorphic ligands

metal, liquid-crystalline ligands] and copper complexes of salicylaldimates<sup>14</sup> [Fig. 13(c); d<sup>9</sup> metal, liquid-crystalline ligands].

Another category of examples would be constituted where the ligand actually had no liquid-crystal phase until complexed, for example *p*-alkoxydithiobenzoates of Ni<sup>II</sup> and Pd<sup>II</sup> [Fig. 14(a)],<sup>15</sup> Rh<sup>I</sup> and Ir<sup>I</sup> 4-alkoxy-*N*-(4'-pyridylmethylene)anilines<sup>16</sup> [Fig. 14(b); L = CO] or, indeed, the Ni<sup>II</sup> and Pt<sup>II</sup> (alkylphenyl)dithiolenes (Fig. 12). It is however, all too easy to have too much of a good thing and, for example, none of the *trans*-bis-[4-alkoxy-*N*-(4'-pyridylmethylene)aniline] complexes of Rh<sup>I</sup> [Fig. 14(b); L = 4-alkoxy-*N*-(4'-pyridylmethylene)aniline] shows a liquid-crystal phase, decomposing at high temperatures instead.

Certain examples of calamitic materials are, however, worthy of further note. Thus, in synthesising palladium(II) complexes of azobenzenes, Ghedini *et al.*<sup>17</sup> were adopting the approach of taking a mesomorphic ligand and binding it to a metal (Fig. 15). The results were, however, remarkable and the flat, almost disc-shaped molecules gave rise to typical rod-like phases. Later work by Espinet *et al.*<sup>18</sup> with related azine ligand systems generated similar results.

A further breakthrough was, however, achieved in the azine complexes when alkanoates were employed to bridge the two palladium centres (Fig. 16). This created a new geometric motif as the complexes now had the shape of a 'partially open book';<sup>19</sup> when chiral carboxylates were used, this resulted in the first examples of metal complexes with a ferroelectric response in the S<sub>C</sub>\* mesophase.†

Another interesting system was that of our alkoxydithiobenzoates complexed to Zn<sup>II</sup>. Analysis by single-crystal X-ray diffraction revealed<sup>15</sup> a dimeric geometry in the solid state, which was shown by extended X-ray absorption fine structure (EXAFS) techniques<sup>20</sup> to persist into the nematic phase at temperatures of 160 °C. This is again an interesting overall shape (Fig. 17) for a molecule which clearly shows calamitic mesomorphism.

Twin drawbacks of many metal-containing liquid-crystal systems are the high temperatures of transition and the tendency to decomposition. Decomposition can even be a problem at low temperatures in some cases but one way of achieving lower temperatures of transition is to reduce the structural anisotropy. This is well illustrated in the following examples. The highly symmetric D<sub>2h</sub> complexes *trans*-[MCl<sub>2</sub>L<sub>n</sub>]<sub>2</sub>, where L<sup>n</sup> = 4-[2-(*p*-alkoxyphenyl)vinyl]pyridine (*n* is the number of carbon atoms in the alkoxy chain), show what few mesophases they possess at elevated temperatures.<sup>21</sup> However, three approaches to reducing the structural anisotropy lead to materials with much more accessible

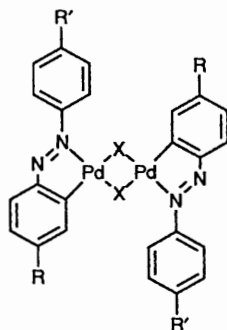


Fig. 15 Orthopalladated diazo complexes

† In S<sub>C</sub>\* phases, the layers are ferroelectric due to the symmetry dropping from C<sub>2h</sub> (S<sub>C</sub>) to C<sub>2</sub> (S<sub>C</sub>\*). As there are two possible directions for the dipolar alignment, then it is possible to switch between them using an applied field, if the sample can be constrained in a suitable environment. Such switching is being used in the new generation 'surface-stabilised ferroelectric liquid-crystal displays.'

mesophases. Thus, for M = Pd, the molecule can be broadened by replacing the Cl ligands with long-chain alkanoates leading to materials with nematic phases (Fig. 18).<sup>21</sup> The structural anisotropy is similarly reduced when one of the ligands L<sup>n</sup> is replaced by a terminal alkene leading to a whole family of materials with sub-100 °C S<sub>A</sub> phases<sup>20</sup> (Fig. 19).

In a similar strategy, we prepared the Rh<sup>I</sup> and Ir<sup>I</sup> complexes *cis*-[MCl(CO)<sub>2</sub>L<sup>n</sup>] (Fig. 20) which show low-temperature (80–130 °C) N and S<sub>A</sub> phases, although the low temperature does not prevent decomposition when M = Rh.<sup>22</sup> We showed, in a related example, that the high-temperature mesophases of the Ag<sup>I</sup> complexes [AgL<sub>2</sub>]<sub>2</sub>X (X = NO<sub>3</sub> or CF<sub>3</sub>SO<sub>3</sub>)<sup>23</sup> (Fig. 21)

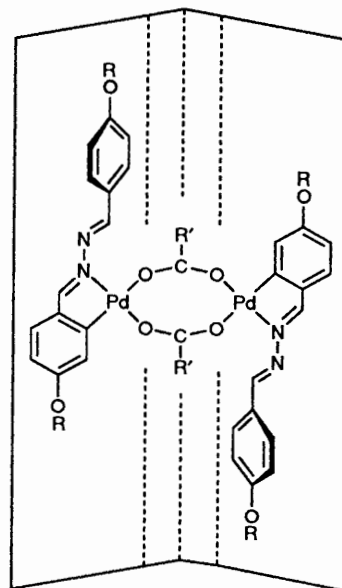


Fig. 16 The 'open-book' geometry in palladium azine systems

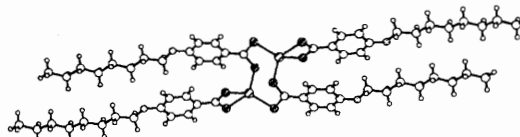


Fig. 17 Molecular structure of tetrakis[(*p*-octyloxy)dithiobenzoato-*S,S'*]dizinc(II)

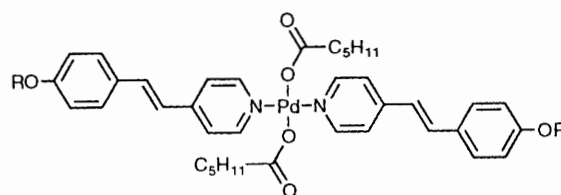


Fig. 18 Mesomorphic Pd<sup>II</sup> complexes with hexanoate ligands

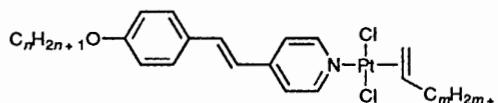


Fig. 19 Mesomorphic Pt<sup>II</sup> alkene complexes

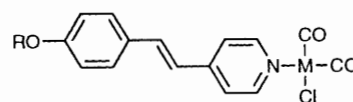
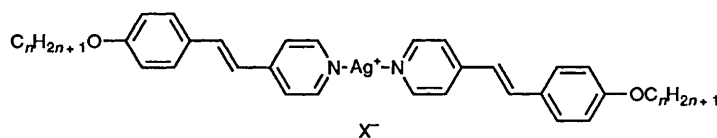


Fig. 20 Mesomorphic Rh<sup>I</sup> and Ir<sup>I</sup> *cis*-[MCl(CO)<sub>2</sub>L<sup>n</sup>] complexes

Fig. 21 Structure of the  $\text{Ag}^{\text{I}}$  complexes  $[\text{AgL}_2]\text{X}$ 

are rendered more accessible by using the much larger alkanesulfate anions  $\text{C}_8\text{H}_{17}\text{OSO}_3$ ,<sup>24</sup>  $\text{C}_{12}\text{H}_{25}\text{OSO}_3$ <sup>25</sup> and  $\text{C}_{14}\text{H}_{29}\text{OSO}_3$ .<sup>26</sup>

Finally in this section, it is worth noting that while it is often true that using chelate ligands can enhance the thermal stability of many complexes, this is not always the case as evidenced by the high thermal stability of the platinum acetylide complexes [Fig. 12(b)] of Takahashi and co-workers.<sup>13</sup>

### Physical Properties

When work first began in this area, researchers were forced to think about the ways in which the metal might modify the properties of liquid-crystal systems. While it is not appropriate here to produce a comprehensive list of such properties, it is pretty certain that factors such as mobile electron density, the ability to tolerate unpaired electron density and of course colour, were at the forefront of the thinking.

**Colour.**—In some ways this is one of the more obvious properties offered by metal complexes and yet full-colour television displays have been made with colourless materials and the use of filters. So where can colour come in? The potential use of colour has been demonstrated in the same way with two related sets of complexes, namely the dithiolenes complexes described by Giroud-Godquin and Mueller-Westerhoff and the dithiobenzoate complexes described by ourselves. The phenomenon of dichroism in molecules is well understood and arises from the selective absorption of polarised light by a molecule in a particular orientation. This fact is used in the so-called Heilmeyer guest-host displays in which contrast is obtained by re-orienting a dye from an absorbing to a non-absorbing orientation. This is achieved by dissolving a few percent of the guest dye in a liquid-crystal host and using the switching properties of the host to control the orientation. This sort of technology offers some advantages over the more conventional (twisted nematic) display configuration in that good contrast is obtained using only one polaroid—this is important as polaroid is one of the more expensive items in the display assembly. However, many of the guest dyes are either photochemically unstable (e.g. azo dyes<sup>27</sup>) while others (e.g. anthraquinones<sup>28</sup>) are less satisfactory as they are effectively disc-shaped molecules dissolved in rod-like solvents and so do not align so well with the solvent molecules.

However, in 1988, Marshall and Jacobs<sup>29</sup> reported an investigation of the complex shown in Fig. 11 ( $n = 4$ ) as a dye using 4-cyano-4'-pentylbiphenyl as the host.<sup>29</sup> The complex had a large absorption coefficient ( $\epsilon = 28\,000\text{ dm}^3\text{ cm}^{-1}\text{ mol}^{-1}$  at 860 nm) and dissolved in the host up to 10% (w/w). The absorbance was then measured in two mutually perpendicular directions representing the optimum and non-optimum absorption directions; at 20 °C, such solutions showed a dichroic ratio ( $R_D$ , defined as  $A_{\parallel}/A_{\perp}$ ;  $A$  = absorbance) of 4.97.

Similar measurements on our alkoxydithiobenzoates of  $\text{Ni}^{\text{II}}$ ,  $\text{Pd}^{\text{II}}$  and  $\text{Zn}^{\text{II}}$  were made difficult by the very low solubility of the complexes in most solvents; thus data were typically obtained at concentrations of <0.5% (w/w). In these experiments the solvents used were the commercial eutectic mixture of cyanobiphenyls and cyanoterphenyls (mixture E7; Merck) for the palladium complexes and the commercial mixture of cyanobicyclohexanes (mixture ZLI2830; Merck) for the nickel and zinc complexes. Each of the nickel(II) and palladium(II) complexes had two absorption bands (ligand based and charge

Table 1 Polarisability data for  $\text{Ir}^{\text{I}}$  complexes  $\text{cis}[\text{IrCl}(\text{CO})_2\text{L}^n]$ 

	$10^{40} \bar{\alpha}/\text{J}^{-1} \text{C}^2 \text{m}^2$	$10^{40} \Delta \alpha/\text{J}^{-1} \text{C}^2 \text{m}^2$
$L^n$ (average)	$35 \pm 4$	$28 \pm 6$
$R = \text{C}_5\text{H}_{11}$	$59 \pm 6$	$54 \pm 10$
$R = \text{C}_7\text{H}_{15}$	$62 \pm 6$	$59 \pm 12$
$R = \text{C}_9\text{H}_{19}$	$60 \pm 6$	$49 \pm 10$

transfer), while the zinc(II) complexes had only one (ligand based); all had high absorption coefficients. We found that  $R_D$  decreased as  $\text{Ni}$  (5.1–6.0) >  $\text{Zn}$  (4.2–4.7) for the ligand-based absorption and as  $\text{Pd}$  (8.7–12.8) >  $\text{Ni}$  (7.0–10.12) for the charge-transfer absorption (the ligand-based absorption of  $\text{Pd}$  was blocked by solvent absorption bands).<sup>30</sup>

The point is then that by choosing highly coloured metal complexes, rod-like dyes can be obtained for dissolution in rod-like hosts, leading in principle to higher solubility and larger dichroic ratios. This is also a case where the very high transition temperatures of these complexes may be of some advantage, as the dichroic ratio increases as the temperature is lowered below the clearing point. Thus, at the temperatures at which these measurements are made (around 20–40 °C), the complexes are well below these clearing points (e.g. 320 °C for  $M = \text{Pd}$ ) and are therefore well ordered.

**Polarisability.**—It is well known that metal atoms have a high density of polarisable electrons. Also properties such as birefringence and dielectric constant depend on polarisability and it is further postulated that the thermal stability of liquid-crystal phases depends to some degree on the polarisability too. Perhaps the clearest example of the influence exerted by a metal in this way is given by our  $\text{Rh}^{\text{I}}$  and  $\text{Ir}^{\text{I}}$  complexes  $\text{cis}[\text{MCl}(\text{CO})_2\text{L}^n]$  (Fig. 20). Thus, measurement of the isotropic polarisability ( $\bar{\alpha}$ ) and the polarisability anisotropy ( $\Delta\alpha$ ) for both the ligands and their  $\text{Ir}^{\text{I}}$  complexes give the results shown in Table 1.

Thus the isotropic polarisability of the ligand nearly doubles on complexation. This is also interesting when comparing the mesomorphism of the ligand with that of the complexes. Thus, while the ligands have a very narrow range  $S_B$  phase, the complexes (which melt at almost the same temperatures) have nematic and  $S_A$  ranges of up to 40 °C. This suggests that these metal fragments [*i.e.*  $\text{cis}[\text{MCl}(\text{CO})_2]$ ] are rather effective in promoting mesomorphic behaviour and this correlates well with ideas generated within the purely organic part of the subject where certain terminal groups are found to have differing abilities to promote the nematic phase. These results seem to suggest that metal complexes may be particularly effective terminal groups in this regard.

**Magnetism.**—By and large, metal complexes form much more stable radicals than organic materials and so several groups have become interested in paramagnetic, metal-containing liquid-crystal systems.

Some of the first systems to be properly examined were the dinuclear copper(II) alkanooates (Fig. 22) where a change in magnetic susceptibility on moving from the crystal to the discotic phase was observed by SQUID magnetometry.<sup>31</sup> Other studies have been carried out on salicylaldimine complexes (Fig. 23) where it was found,<sup>32–34</sup> for example, that while the

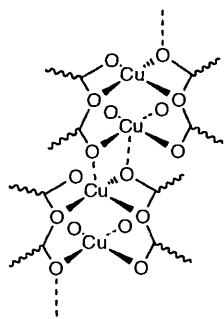


Fig. 22 Structure in the mesophase of copper(II) alkanoates

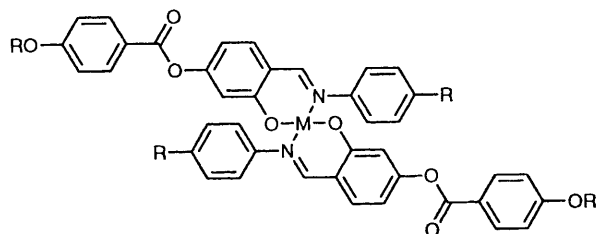


Fig. 23 Salicylaldehyde complexes

magnetic anisotropy was positive for the vanadyl complexes, it was negative for the copper derivatives (a 'positive' anisotropy means that the susceptibility along the long molecular axis is greater than that perpendicular to it; a negative anisotropy implies the opposite). Further, the vanadyl complexes were readily aligned in a magnetic field.<sup>33</sup>

While several other paramagnetic complexes have been described,<sup>35</sup> there is little prospect of the paramagnetism being utilised in switching until the unpaired electron density can be effectively spin-orbit coupled, because if the magnetism is not spin-orbit coupled then changing the magnetic field direction will affect the unpaired electron(s) but not the molecule as a whole (*i.e.* the spin can be regarded as being essentially isotropic). The prospect of ferromagnetic systems is also of interest.<sup>36</sup>

### Other Effects in Metal-containing Systems

Having discussed some of the physical properties which are modified by inclusion of a metal, it is worth considering and compiling the evidence concerning the occurrence and significance of intermolecular metal-metal or metal-ligand interactions in the mesophases of metal-containing liquid-crystal systems, as there have been some suggestions that such interactions are essential to the formation of liquid-crystal phases in metal complexes.

Perhaps the first mention of intermolecular interactions was by Giroud-Godquin and Mueller-Westerhoff who had found that while nickel and platinum derivatives of (alkylphenyl)dithiolenes (Fig. 12) were mesomorphic, the palladium derivatives were not. By comparison with the known crystal structures of the unsubstituted dithiolenes of Pd and Pt, where M-M distances of 2.79 and 2.77 Å (respectively) were observed, the lack of mesomorphism was attributed to strong Pd-Pd 'bonds'. While it is certainly difficult to account for the non-mesomorphic nature of the palladium derivatives, in the absence of crystallographic and EXAFS evidence, it is difficult to 'pin the blame' on Pd-Pd interactions, especially as similar M-M interactions are also implied for the platinum complexes. Nevertheless, the notion of Pd-Pd interactions suppressing mesomorphism perpetuated for some time in the literature.

That intermolecular interactions might be present in mesophases has been the subject of speculation by several authors and there is one example where an intermolecular Cu-Cu correlation was found in a  $S_B$  phase by EXAFS.<sup>37</sup> However,

there are several examples in the literature where phase diagrams have been constructed of binary mixtures of a mesomorphic metal complex and a mesomorphic organic compound in order to establish the identity of certain phases (co-miscibility of two mesophases is proof of their identity, although non-miscibility provides no information). If particular intermolecular M-M or M-L interactions were important for mesophase formation, these should be diluted out at high percentages of the organic compound leading to unexpected features in the phase diagram. No such behaviour has yet been observed, although a more systematic study using a variety of techniques would answer these questions more fully.

The necessity for intermolecular M-M or M-L interactions to stabilise the mesophases of metal complexes would imply that there is one type of nematic or smectic phase for organics, and another for metal complexes. It is the author's view that this is extremely unlikely, and indeed that it is probably disproved by the existence of mesophases in various ferrocene derivatives where there are no co-ordination sites available at the metal<sup>38</sup> and hence no possibility for such interactions.

However, that such intermolecular interactions are not essential does not preclude their existence. Thus, the dinuclear copper(II) carboxylates,<sup>39</sup>  $[\text{Cu}_2(\text{O}_2\text{CR})_4]$  (and their rhodium analogues), exist as pseudo polymers in both the solid state and the (discotic hexagonal) mesophase by virtue of intermolecular M-O interactions (Fig. 22) as found by EXAFS techniques.<sup>40</sup> The necessity for these interactions in systems of this type is shown by the fact that the related dithiobenzoates,  $[\text{Cu}_2(\text{S}_2\text{-CC}_6\text{H}_4\text{OC}_n\text{H}_{2n+1})_4]$ , are non-mesomorphic due to the weak nature of the intermolecular Cu-S interactions.<sup>41</sup>

### What Next?

This area of research is growing and new, interesting materials and observations are continually being reported. There are, however, many unexploited areas such as the marriage between liquid-crystalline cell membranes and liquid-crystalline metal complexes. Similarly, there is the idea of catalysis and reactivity by metal complexes (liquid-crystalline or not) in liquid-crystal solvents. The field is maturing fast and awaits the input of many who would not even have considered it worthwhile or interesting. Go on, try it! It's fun!

### Acknowledgements

Figures 1, 2, 3, 5, 6, 11, 16 and 22 were reproduced from ref. 1(a) with permission from Wiley.

### References

- (a) D. W. Bruce, in *Inorganic Materials*, eds. D. W. Bruce and D. O'Hare, Wiley, Chichester, 1992; (b) P. Espinet, M. A. Esteruelas, L. A. Oro, J. L. Serrano and E. Sola, *Coord. Chem. Rev.*, 1992, **117**, 215; (c) A.-M. Giroud-Godquin and P. M. Maitlis, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 402; (d) S. A. Hudson and P. M. Maitlis, *Chem. Rev.*, 1993, **93**, 861.
- J. W. Goodby, *J. Mater. Chem.*, 1991, **1**, 307.
- K. J. Toyne, in *Thermotropic Liquid Crystals*, ed. G. W. Gray, Wiley, Chichester, 1987.
- D. Demus, *Liq. Cryst.*, 1989, **5**, 75; H. Ringsdorf, B. Schlarb and J. Venzmer, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 113.
- See for example, J. Simon and C. Sirlin, *Pure Appl. Chem.*, 1989, **61**, 1625.
- See for example, G. Lattermann, S. Schmidt, R. Kleppinger and J.-H. Wendorff, *Adv. Mater.*, 1992, **4**, 30.
- See for example J.-M. Lehn, J. Malthête and A.-M. Levelut, *J. Chem. Soc., Chem. Commun.*, 1985, 1794.
- (a) B. A. Gregg, M. A. Fox and A. J. Bard, *J. Chem. Soc., Chem. Commun.*, 1987, 1134; (b) *J. Am. Chem. Soc.*, 1989, **111**, 3024; (c) *J. Phys. Chem.*, 1989, **93**, 4227.
- M. J. Cook, S. J. Cracknell and K. J. Harrison, *J. Mater. Chem.*, 1991, **1**, 703.

- 10 C. Sirlin, L. Bosio and J. Simon, *Mol. Cryst., Liq. Cryst.*, 1988, **155**, 231; *J. Chem. Soc., Chem. Commun.*, 1987, 379.
- 11 U. T. Mueller-Westerhoff, A. Nazzal, R. J. Cox and A.-M. Giroud, *Mol. Cryst., Liq. Cryst.*, 1980, **56**, 249; A.-M. Giroud, A. Nazzal and U. T. Mueller-Westerhoff, *Mol. Cryst., Liq. Cryst.*, 1980, **56**, 225.
- 12 D. W. Bruce, E. Lalinde, P. Styring, D. A. Dunmur and P. M. Maitlis, *J. Chem. Soc., Chem. Commun.*, 1986, 581; H. Adams, N. A. Bailey, D. W. Bruce, D. A. Dunmur, E. Lalinde, M. Marcos, C. Ridgway, A. J. Smith, P. Styring and P. M. Maitlis, *Liq. Cryst.*, 1987, **2**, 381.
- 13 T. Kaharu, H. Matsubara and S. Takahashi, *J. Mater. Chem.*, 1991, **1**, 145; 1992, **2**, 43.
- 14 See for example, M. Marcos, P. Romero, J. L. Serrano, C. Bueno, J. A. Cabeza and L. A. Oro, *Mol. Cryst., Liq. Cryst.*, 1989, **167**, 123; M. Marcos, P. Romero and J. L. Serrano, *Chem. Mater.*, 1990, **2**, 495; N. Hoshino, H. Murakami, Y. Matsunaga, T. Inabe and Y. Maruyama, *Inorg. Chem.*, 1990, **29**, 1177.
- 15 H. Adams, A. C. Albeniz, N. A. Bailey, D. W. Bruce, A. S. Cherodian, R. Dhillon, D. A. Dunmur, P. Espinet, J. L. Feijoo, E. Lalinde, P. M. Maitlis, R. M. Richardson and G. Ungar, *J. Mater. Chem.*, 1991, **1**, 843.
- 16 M. A. Esteruelas, E. Sola, L. A. Oro, M. B. Ros and J.-L. Serrano, *J. Chem. Soc., Chem. Commun.*, 1989, 55; M. A. Esteruelas, E. Sola, L. A. Oro, M. B. Ros, M. Marcos and J.-L. Serrano, *J. Organomet. Chem.*, 1990, **387**, 103.
- 17 M. Ghedini, M. Longeri and R. Bartolino, *Mol. Cryst., Liq. Cryst.*, 1982, **84**, 207; M. Ghedini, S. Licoccia, S. Armentano and R. Bartolino, *Mol. Cryst., Liq. Cryst.*, 1984, **108**, 269; M. Ghedini, S. Armentano and F. Neve, *Inorg. Chim. Acta*, 1987, **134**, 23; M. Ghedini, S. Licoccia, S. Armentano and R. Bartolino, *Mol. Cryst., Liq. Cryst.*, 1984, **108**, 269.
- 18 P. Espinet, E. Lalinde, M. Marcos, J. Pérez and J. L. Serrano, *Organometallics*, 1990, **9**, 555.
- 19 P. Espinet, J. Etxebarria, M. Marcos, J. Pérez, A. Rémon and J. L. Serrano, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 1065.
- 20 D. Guillon, D. W. Bruce, P. Maldivi, M. Ibn-Elhaj and R. Dhillon, *Chem. Mater.*, submitted.
- 21 J. P. Rourke, F. P. Fanizzi, D. W. Bruce, D. A. Dunmur and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 1992, 3009; J. P. Rourke, F. P. Fanizzi, N. J. S. Salt, D. W. Bruce, D. A. Dunmur and P. M. Maitlis, *J. Chem. Soc., Chem. Commun.*, 1990, 229.
- 22 D. W. Bruce, D. A. Dunmur, M. A. Esteruelas, S. E. Hunt, R. Le Lagadec, P. M. Maitlis, J. R. Marsden, E. Sola and J. M. Stacey, *J. Mater. Chem.*, 1991, **1**, 251.
- 23 D. W. Bruce, D. A. Dunmur, S. A. Hudson, P. M. Maitlis and P. Styring, *Adv. Mater. Opt. Electron.*, 1992, **1**, 37.
- 24 H. Adams, N. A. Bailey, D. W. Bruce, S. C. Davis, D. A. Dunmur, S. A. Hudson and S. J. Thorpe, *J. Mater. Chem.*, 1992, **2**, 395.
- 25 D. W. Bruce, D. A. Dunmur, S. A. Hudson, E. Lalinde, P. M. Maitlis, M. P. McDonald, R. Orr, P. Styring, A. S. Cherodian, R. M. Richardson, J. L. Feijoo and G. Ungar, *Mol. Cryst., Liq. Cryst.*, 1991, **206**, 79.
- 26 D. W. Bruce and J. A. Bell, unpublished work.
- 27 D. Vorländer, *Trans. Faraday Soc.*, 1933, **12**, 907.
- 28 M. G. Pellatt, I. H. C. Roe and J. Constant, *Mol. Cryst., Liq. Cryst.*, 1980, **59**, 299.
- 29 K. L. Marshall and S. D. Jacobs, *Mol. Cryst., Liq. Cryst.*, 1988, **159**, 181.
- 30 D. W. Bruce, D. A. Dunmur, S. E. Hunt, P. M. Maitlis and R. *J. Mater. Chem.*, 1991, **1**, 857.
- 31 A.-M. Giroud-Godquin, J.-M. Latour and J.-C. Marchon, *It Chem.*, 1985, **24**, 4452.
- 32 N. Hoshino, A. Kodama, T. Shibuya, Y. Matsunaga and S. Miyajima, *Inorg. Chem.*, 1991, **30**, 3091.
- 33 J. L. Serrano, P. Romero, M. Marcos and P. J. Alonso, *J. Chem. Soc., Chem. Commun.*, 1990, 859.
- 34 M. Marcos, P. Romero and J.-L. Serrano, *J. Chem. Soc., Chem. Commun.*, 1989, 1641.
- 35 See for example, Yu. G. Galyametdinov, G. I. Ivanova and I. V. Ovchinnikov, *Zh. Obshch. Khim.*, 1984, **54**, 2796; Yu. G. Galyametdinov, D. Z. Zakieva and I. V. Ovchinnikov, *Izv. Akad. Nauk. SSSR Ser. Khim.*, 1986, 491; Yu. G. Galyametdinov, G. I. Ivanova and I. V. Ovchinnikov, *Izv. Akad. Nauk. SSSR Ser. Khim.*, 1989, 1931; S. Chandrasekhar, B. R. Ratna, B. K. Sadashiva and V. N. Raja, *Mol. Cryst., Liq. Cryst.*, 1988, **165**, 123; P. Styring, S. Tantrawong, D. R. Beattie and J. W. Goodby, *Liq. Cryst.*, 1991, **4**, 581.
- 36 See O. Khan, Y. Pei and Y. Journaux, in *Inorganic Materials*, eds. D. W. Bruce and D. O'Hare, Wiley, Chichester, 1992.
- 37 G. Albertini, A. Guido, G. Mancini, S. Stizza, M. Ghedini and R. Bartolino, *Europhys. Lett.*, 1990, **12**, 629.
- 38 See for example, J. Bhatt, B. M. Fung, K. M. Nicholas and C.-D. Poon, *J. Chem. Soc., Chem. Commun.*, 1988, 1439; M. A. Khan, J. C. Bhatt, B. M. Fung, K. M. Nicholas and E. Wachtel, *Liq. Cryst.*, 1989, **5**, 285; P. Singh, M. D. Rausch and R. W. Lenz, *Liq. Cryst.*, 1991, **9**, 19.
- 39 A.-M. Giroud-Godquin, J.-C. Marchon, D. Guillon and A. Skoulios, *J. Phys. Lett (Paris)*, 1984, **45**, 681; H. Abied, D. Guillon, A. Skoulios, A.-M. Giroud-Godquin and J.-C. Marchon, *Liq. Cryst.*, 1987, **2**, 269.
- 40 H. Abied, D. Guillon, A. Skoulios, H. Dexpert, A.-M. Giroud-Godquin and J.-C. Marchon, *J. Phys. France*, 1988, **49**, 345; P. Maldivi, D. Guillon, A.-M. Giroud-Godquin, J.-C. Marchon, H. Abied, H. Dexpert and A. Skoulios, *J. Chim. Phys.*, 1989, **86**, 1651.
- 41 D. W. Bruce and R. Le Lagadec, unpublished work.

Received 19th March 1993; Paper 3/01604H