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Transition metal liquid crystals: advanced materials within the reach of the coordination chemist

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A. INTRODUCTION

The ubiquitous presence of liquid crystal displays (LCD) has made liquid crystals perhaps the most popular and familiar class of advanced materials in modern life. In contrast with this popularity, the rather specific character of the field and its absence from the usual academic curricula has kept even its basic principles unknown to most chemists, unless they have happened to get involved in it at the research level. In recent years, these materials have given rise to important technological innovations. The advances extend to fields as diverse as electro-optical displays, temperature-sensing devices, high performance polymers, etc. [1]. The logical industrial interest has caused an enormous increment in research on mesogenic compounds.

Until 1980, most of the reported mesogenic materials were organic compounds. The versatility of organic chemistry allowed the consecution of a bewildering variety of chemical structures that meet the electronic and geometric requirements necessary to produce a liquid crystal [2–4]. Very recently, during the last decade, a new class of mesogens incorporating transition metals has burst into the field. Until now, most of these new transition metal liquid crystals (TMLC) have been of only academic interest, but their properties have brought about expectations that are attracting an increasing number of researchers.

It is hoped that this review will serve to open the field to many coordination chemists who can use their specific expertise to generalise and develop metallomesogenic systems based on other ligands and other metals. Those sensitive to the appeal of the topic will have to take into account some peculiarities of the coordination chemistry in liquid crystals, and will possibly like to know some aspects that can be particularly interesting to get into, and to have a quick access to what is already known or has already been made in this field. For this reason, the review is organised in a way that we hope will serve all these needs. It starts with a short introduction to the basic principles of liquid crystals and their jargon. This is followed by a comprehensive collection of results published up to June 1991 classified according to the d^n electronic configuration of the metal ion, which is complemented by an alternative entry to literature by type of ligand in tabular form. The review closes with a section containing some personal views of the present and prospects of TMLC, a kind of "what, how and why" in TMLC that we hope will be of use to the reader. For a less detailed but more general view of the broader field of metallomesogens (which includes mesogenic compounds of non-transition metals), the reader is referred to a recent article by Giroud-Godquin and Maitlis [5], which discusses compounds which appeared up to early 1990 arranged by ligand type.

(i) Basic concepts in liquid crystals

Liquid crystals (or mesogenic compounds) are materials which show liquid crystallinity (or mesomorphism). This behaviour appears under given conditions when phases that do not correspond to an ordered solid nor to a disordered liquid or solution are formed; these intermediate phases are called *mesophases*. Liquid crystals have been defined as "orientationally ordered" liquids or "positionally disordered" crystals [6] and combine properties of both the crystalline (optical and electrical anisotropy) and the liquid (molecular mobility and fluidity) states. There are two different ways of taking a crystal to a mesophase, corresponding to two broad families of liquid crystals, namely:

(a) By heating the crystalline solid or cooling the isotropic liquid: In this case, the liquid crystal is termed *thermotropic*. When the thermotropic mesophase appears both in the heating and in the cooling process (i.e. when it is thermodynamically stable) it is called *enantiotropic*. The thermodynamically unstable mesophases, which only appear in the cooling process due to the hysteresis in the crystallization point, are referred to as *monotropic*.

(b) By dissolving the compound in an adequate solvent under given concentration and temperature conditions. These are known as *lyotropic* liquid crystals.

A large number of compounds have been described as thermotropic or lyotropic liquid crystals, and some of them exhibit both types of behaviour (*amphotropic* liquid crystals). Thermotropic liquid crystals have gained a relevant place in the field of materials science, whereas lyotropic liquid crystals are fundamental in life science. Both kinds of self-organizing system play an important role in supramolecular chemistry [7].

In mesogenic materials, the intermolecular forces responsible for the molecular arrangement are essentially the same as those operating in molecular solids. However, only certain molecules show liquid crystal behaviour. Mesogenic molecules need to meet a series of structural and electronic requirements [8] so that a satisfactory packing of molecules is achieved with appropriate interactions between neighbouring molecules. The existence of permanent dipole moments and their magnitude or the anisotropy of the molecular polarizability are determinant in the efficacy of these molecular interactions.

Taking into account structural factors, thermotropic liquid crystals are classically classified in two main groups, *calamitic* (rod-like) and *discotic* (disc-like). A representative example of each type is shown in Fig. 1. In both cases, the molecules can be described as cylinders with a large anisotropy. Calamitic compounds show a structure where the axial component is larger than the radial ones (Fig. 2(a)). On the other hand, radial components are the larger in discotic molecules (Fig. 2(b)). Using these theoretical models, the phase transitions shown by a high number of low and high molecular weight mesogens have been successfully explained. In the last few years, an increasing number of new mesogenic compounds which do not fit these

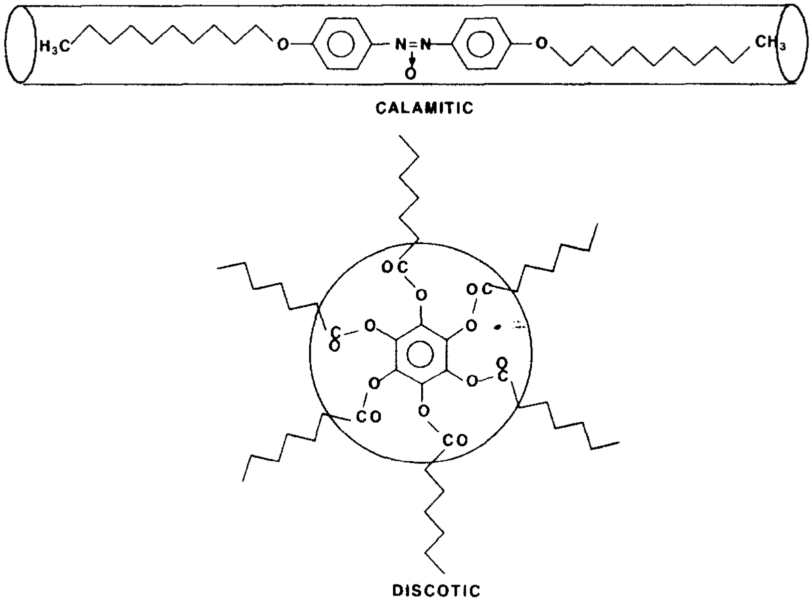

Fig. 1. Representative examples of calamitic and discotic molecules.

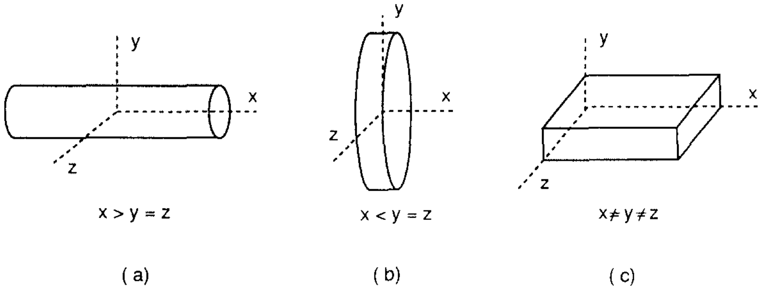

Fig. 2. Three geometrical models of different mesogenic compounds.

models has been described: molecules that combine both calamitic and discotic shapes (phasmidic compounds), calamitic and discotic twins, compounds with very large lateral substituents, etc. New theoretical models have been proposed in order to explain the mesogenic behaviour of these materials [2] (Fig. 2(c)).

Lyotropic liquid crystals [9] can also be described by a simple model. Such molecules usually possess the amphiphilic character typical of compounds with tensoactive properties, consisting of a polar head and one or several aliphatic chains. The polar head is formed by an ionic group, either cationic or anionic, or by one or more groups having strong dipole moments which can interact with polar solvents. A representative example of the former is sodium stearate (soap) (Fig. 3(a)); the latter

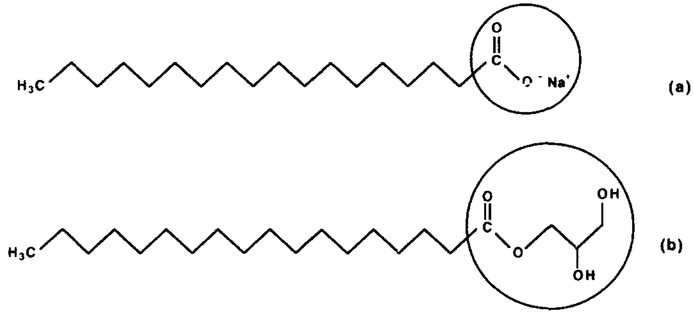

Fig. 3. Two representative examples of lyotropic ligand crystal compounds.

can be illustrated by glycerylmonostearate (Fig. 3(b)). Both compounds form mesophases in aqueous solutions.

The vast majority of thermotropic mesogens described are covalent materials, whereas most of the lyotropic are ionic.

The three basic types of structure described above are associated with three basic types of mesophase in which the molecular geometry determines the resulting molecular arrangement: calamitic, discotic and lyotropic mesophases.

Calamitic mesophases [10,11]. There are two types of calamitic mesophase: *nematic* mesophase and *smectic* mesophase (or lamellar).

The less ordered mesophase is the nematic mesophase (N). In this, the main axis of the molecules align along a preferred direction which is called the *director*, $\vec{n}$. The molecules can move within the nematic mesophase and rotate around their main axis, but in spite of this freedom of movement they tend to keep aligned (Fig. 4(a)).

The smectic mesophases (S) show a higher degree of order. In such mesophases the molecules orient, as in the nematic mesophase, with their main axis parallel to the director $\vec{n}$, but they also form layers. These layers can be perpendicular to the director (as in the S_A phase) or not (tilted phases) (Fig. 4(b)). The S_A and S_C phases are the less ordered and more common smectic mesophases. Due to their molecular mobility and their low viscosity, they are called fluid mesophases. In addition, there are other types of smectic phases that show tri-dimensional order, a restricted molecular mobility and greater viscosities. These mesophases are known as crystalline mesophases. Two representative examples of the latter are the S_B and S_G where, in addition to the order shown by the fluid smectic phases, the molecules show a hexagonal positional arrangement (Fig. 4(c)).

A particular case of both kinds of phase appears when the molecule is chiral. Chirality in nematogenic molecules causes a twist in the nematic arrangement, giving rise to the cholesteric phase. Its structure consists of nematic layers whose successive individual directors describe a helical structure (Fig. 5(a)). Equivalent layers appear after a 2π angle and the distance between them defines the pitch of the helix. Chiral

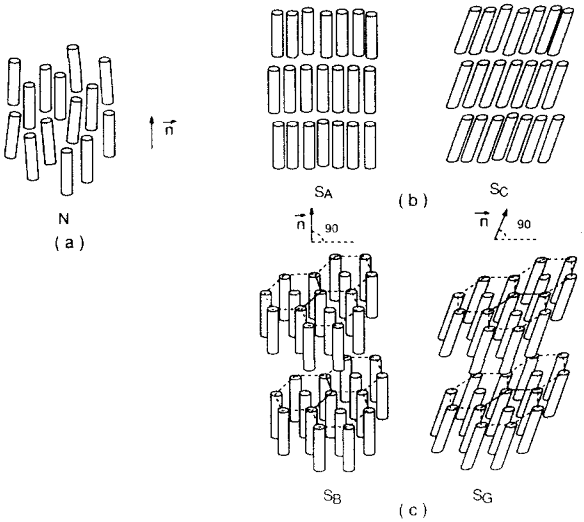

Fig. 4. Schematic representation of calamitic mesophases: N, nematic; S_A, smectic A; S_C, smectic C; S_B, smectic B; S_G, smectic G.

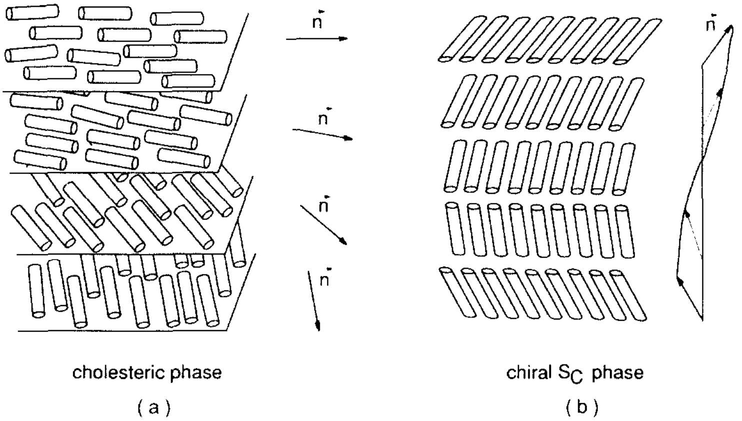

Fig. 5. Schematic representation of two chiral phases.

molecules in the S_C phase (or in other fluid tilted phases) produce a twisted structural variant (Fig. 5(b)). Cholesteric and smectic chiral phases show optical activity and selective reflection, and the latter exhibit ferroelectric properties.

Discotic mesophases [12]. Two different classes of discotic mesophase can be defined: columnar and nematic mesophases. In the latter, the arrangement of the disc-like molecules is similar to the ordinary nematic phase of rod-like molecules (Fig. 6(a)). Nevertheless, a columnar local order remains in the fluid mesophase. In columnar mesophases, the molecules pile up in parallel columns which form a periodic two-dimensional array. Several types of arrangement are possible in this

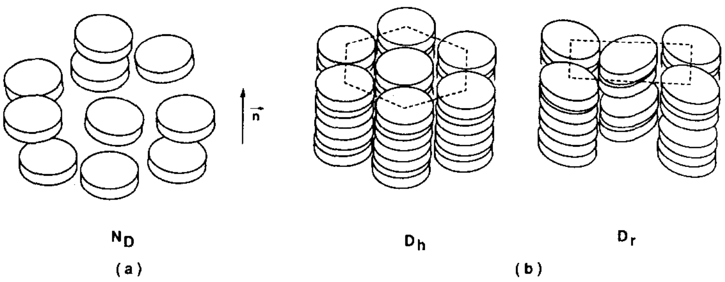

Fig. 6. Schematic representation of three typical discotic phases: N_D, discotic nematic; D_h, hexagonal columnar; D_r, rectangular columnar.

kind of compound. Two significant examples, the hexagonal discotic phase and the rectangular discotic phase are represented in Fig. 6(b).

Lyotropic mesophases [13]. In lyotropic phases, a new parameter must be considered: the solvent. As a result, not only temperature but also the number of components in the solution and their concentrations are decisive factors in the appearance of these mesophases. Depending on the concentration, different types of micelle can be formed which will influence the type of micellar arrangement in the mesophase. Three representative examples of lyotropic mesophases are (Fig. 7): (a) the neat phase, very frequent in binary amphiphile/water systems, which is isostructural with the S_A phase and involves plate-shaped micelles; (b) the cubic isotropic phase, which consists of spherical micelles packed in a body-centred cubic lattice; and (c) the middle phase, which involves cylindrical micelles in a hexagonal array similar to that observed in S_B thermotropic phases.

The characterization of the mesophases formed by liquid crystalline materials can be achieved by different means, or more usually by a combination of them. The most used and classic is the observation of the texture* [14] shown by the mesophase

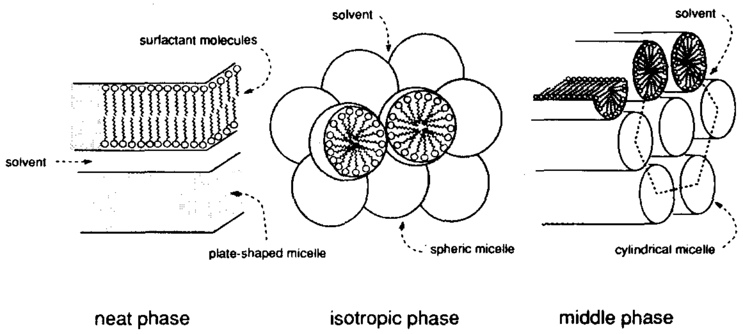

Fig. 7. Schematic representation of some typical lyotropic phases.

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* Texture: picture of a thin layer of liquid crystal observed by means of a microscope, usually with polarized light.

in a polarizing microscope equipped with a hot stage. Each mesophase exhibits one or several characteristic textures; their study over several heating and cooling cycles allows, in favourable cases, the unambiguous characterization of the phase [10,11]. However, this simple method is, in many cases, insufficient and needs the support of other techniques such as X-ray diffraction [12,15] on the mesophase, miscibility tests [16], etc. Calorimetric methods [17] are applied for the determination of the thermic and thermodynamic variables involved in the phase transition, but are of little use for mesophase identification. Usually, only a combination of several methods allows a safe identification of the mesophase.

Some other methods can be of great utility in the study of the mesophases exhibited by certain compounds. Examples of such techniques are nuclear magnetic resonance [18] and electronic microscopy [19], useful in lyotropic liquid crystals; electronic spin resonance, applied to paramagnetic mesogens; neutron scattering; vibrational spectroscopy [20]; etc.

B. d^1-d^5 ELECTRONIC CONFIGURATIONS

Mononuclear complexes of d^1 to d^5 electronic configurations can show a wide range of coordination numbers, although the most common stereochemistries are tetrahedral and octahedral. At first glance none of these stereochemistries are specially adequate for achieving mesogenic properties and thus ions with these configurations have not been extensively used.

Complexes shown in Fig. 8 can be prepared by reaction of vanadyl acetate or sulphate with the corresponding salicylideneamine under refluxing ethanol [21]. Spectroscopic data suggest a square-pyramidal geometry about the vanadium atom, as is usually found in VO^{2+} complexes with two chelating ligands [22]. The mesophase obtained for these complexes depends on the nature of the substituents R_1 and R_2. The complex with $R_1 = OC_7H_{15}$ and $R_2 = C_6H_4$-4-OC_8H_{17} shows a smectic A mesophase [21], whereas complexes with $R_1 = O_2C-C_6H_4$-4-$OC_{10}H_{21}$ and several alkyl and aryl R_2 groups show nematic and smectic mesophases that have been characterized by X-ray diffraction [23]. These mesogenic complexes are paramagnetic, according to the d^1 configuration of the metallic centre, showing positive anisotropy of the magnetic susceptibility and being easily oriented in their nematic phase in the presence of magnetic fields.

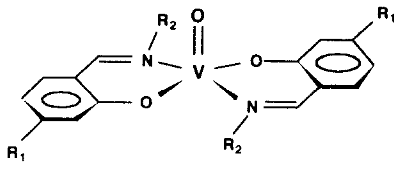


Fig. 8.

Galyametdinov et al. have reported the synthesis and mesogenic behaviour of the Fe(III) complex of Fig. 9, which shows a paramagnetic S_A mesophase between 85 and 151°C [24]. Additionally, the octahedral β-diketonate complex [Fe-(RCOCHCOR)$_3$] (R = C_6H_4–4-$C_{10}H_{21}$) has been described as "possibly" mesogenic, although no details or evidence of its mesogenic behaviour have been given [25].

Dinuclear complexes from Group VI metals with long chain carboxylate ligands have recently been prepared [26]. The complexes have a quadruple metal–metal bond and a "lantern" structure. Cr(II) and Mo(II) derivatives show a hexagonal columnar mesophase, whereas W(II) complexes are not mesogenic. This difference has been tentatively related to the relative strength of the M···O intermolecular interactions, on the basis of calorimetric data. A detailed description of the columnar mesophase of these dinuclear carboxylate complexes will be given in Sect. F.

C. d^6 ELECTRONIC CONFIGURATION

In spite of the great number of transition metals forming stable ions with a d^6 electronic configuration, mesogenic complexes of these ions are very rare. Only some iron(II) and ruthenium(II) mesogens have been reported.

(i) Iron(II) complexes

Among the mesogenic compounds whose molecular geometries differ more from those that typically give rise to liquid crystallinity are those derived from ferrocene. The first examples (Fig. 10), reported by Malthete and Billard, were obtained by condensation of 4-substituted benzaldehydes with *p*-(ferrocenylcarboxy)aniline [27]. These complexes display smectic mesomorphism.

Complexes substituted in both cyclopentadienyl rings have been prepared by reaction of [Fe(C_5H_4–COCl)$_2$] with the corresponding 4-alkyloxy-4′-biphenols [28] (Fig. 11). It has not been discovered whether these molecules adopt a "U" (shown) or an "S" geometry. Complexes with $n = 5$ or 6 show monotropic S_C mesophases, whereas the $n = 11$ complex shows an S_A mesophase, also monotropic. For these

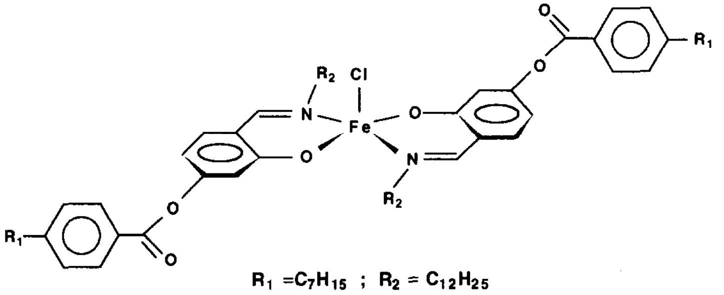


Fig. 9.

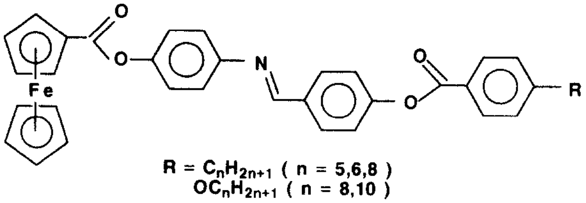


Fig. 10.

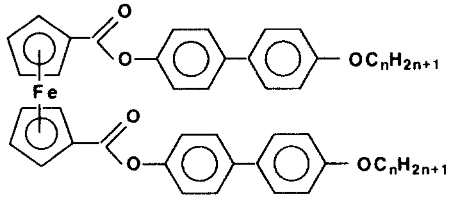


Fig. 11.

derivatives, the presence of only one mesogenic substituent on ferrocene, as in Fig. 10, failed to induce mesomorphism.

(ii) Ruthenium(II) complexes

Complexes of formula $[Ru_2(\mu\text{-}O_2C{-}C_nH_{2n+1})_4]$ can be synthesized by reducing the mixed-valence complex $[Ru^{II}Ru^{III}Cl(\mu\text{-}O_2C{-}C_nH_{2n+1})_4]$ with a Cr(II) salt, followed by ligand exchange with the appropriate carboxylic acid [29]. These dinuclear complexes with a double metal–metal bond have two unpaired electrons at room temperature. The columnar mesophase found for these compounds is similar to that shown by Group VI metal complexes, which had a similar "lantern" structure. The parent mixed-valence complexes $[Ru^{II}Ru^{III}(\mu\text{-}O_2C{-}C_nH_{2n+1})_5]$ [30] show a paramagnetic hexagonal columnar mesophase above 130°C. It has been suggested that, in the mesophase, the anionic alkanoates bridge dimeric cationic units within the columns.

D. d^7 ELECTRONIC CONFIGURATION

Mononuclear coordination compounds of this electronic configuration are virtually confined to those of Co(II), which are easily oxidized to the corresponding Co(III) derivatives. In addition, this electronic configuration can be found in some dinuclear Rh(II) and Ir(II) compounds.

(i) Cobalt(II) complexes

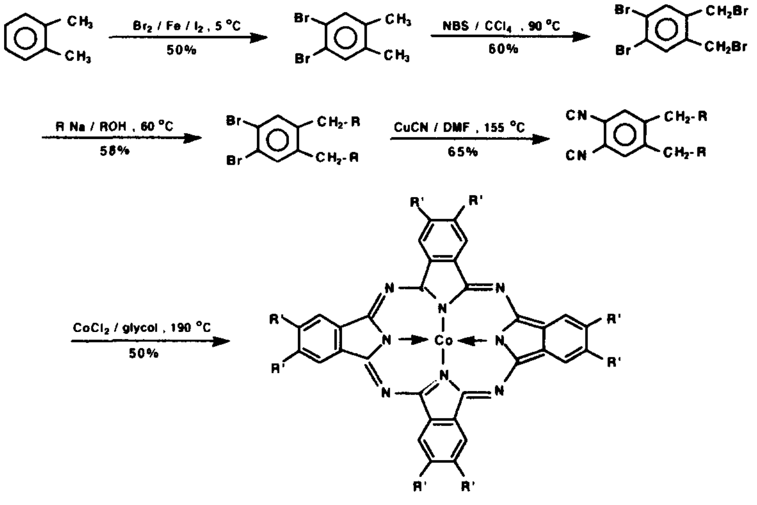
Mesogenic cobalt(II) complexes can be prepared by using substituted phthalocyanines as ligands. It will be shown in the following sections that this kind of tetradentate macrocyclic ligand is capable of forming mesogenic complexes with several M(II) ions; the complexes show mesophases similar to those obtained for the free ligands, but at noticeably higher temperatures.

Scheme 1 illustrates the general procedure for obtaining substituted phthalocyanines and their cobalt complexes; in particular, mesogenic complexes are obtained when $R' = CH_2OC_nH_{2n+1}$ [31]. The compound with $n = 8$ shows a mesophase identified as a discotic columnar mesophase on the basis of its microscopic textures. Reaction of this complex with NaCN in ethanol in the presence of air yields an anionic Co(III) complex with two axial CN ligands. This complex eliminates NaCN when treated with hot water, yielding the polymeric Co(III) compound shown in Scheme 2. Both Co(III) compounds are mesogenic, showing the same columnar mesophase observed in their Co(II) precursor, although at higher temperatures.

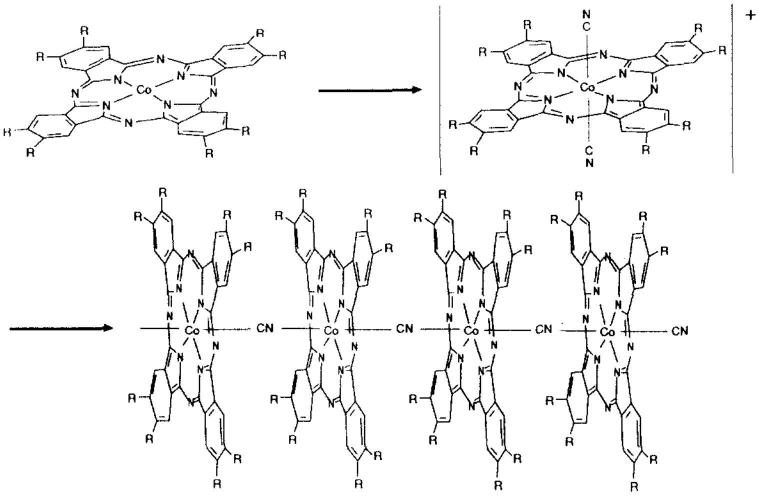
Apart from these phthalocyanine complexes, some other mesogenic Co(II) complexes with macrocyclic porphyrin ligands have recently been reported [32,33].

(ii) Rhodium(II) complexes

Despite the scarcity of Rh(II) complexes, this oxidation state is found in a number of compounds containing carboxylates as ligands [34]. Figure 12 shows the molecular structure of the adduct $[Rh_2(\mu\text{-}O_2CCH_3)_4] \cdot 2H_2O$. These dimeric carbox-



Scheme 1. General procedure for obtaining substituted phthalocyanine cobalt complexes.



Scheme 2. Procedure for obtaining mesogenic Co(III) polymer derivatives using substituted phthalocyanine Co(II) complexes as precursors

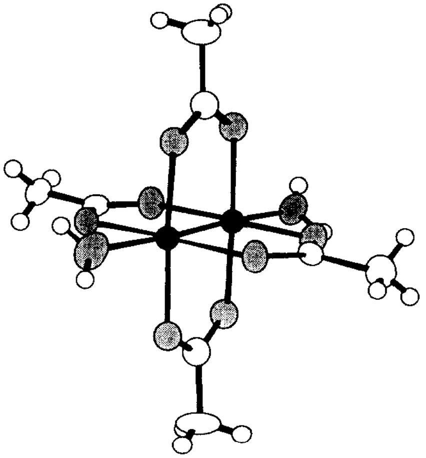


Fig. 12. Structure of $[Rh_2(\mu\text{-}O_2CCH_3)_4]\cdot 2H_2O$. Adapted from ref. 34.

ylate Rh(II) complexes are diamagnetic and consequently contain a single Rh—Rh bond [35] ($d_{Rh-Rh} = 2.39$ Å for acetate).

Mesogenic complexes of similar structure can be obtained, as we have already mentioned for Ru(II), Cr(II) and Mo(II), by using carboxylate ligands derived from fatty acids of various lengths. The synthesis of these complexes is achieved by an exchange reaction between dirhodium tetraacetate and the appropriate fatty acid ($HO_2C{-}C_nH_{2n+1}$), when heating the mixture at 120°C for 2 h. Alkanoate complexes with $n = 4$–23 exhibit a mesophase, identified by X-ray analysis as a columnar mesophase characterized by a two-dimensional hexagonal lattice (D_{ho}) [36]. For $n=3$, the existence of a monotropic rectangular columnar mesophase has been suggested [37]. Recently, Poizat et al. have reported on Raman spectroscopy as a highly sensitive probe of the phase transitions exhibited by these metal–metal-bonded rhodium(II) mesogens [38].

Isostructural Rh(II) complexes obtained with 4-alkyloxybenzoate ligands ($O_2C{-}C_6H_4{-}4{-}OC_nH_{2n+1}$) also show columnar mesomorphism for $n \geqslant 10$ [39]. Structural analysis of this mesophase revealed that the columns adopt a two-dimensional rectangular arrangement (spatial group Cmmm). This ordered rectangular columnar mesophase is unprecedented even within organic mesogens. The complexes obtained with benzoate ligands containing three alkyloxy chains in the 3,4,5 positions of the benzoate ring exhibit a disordered hexagonal columnar mesophase (D_{hd}), whereas the complex containing two-chained benzoate ligands displays both rectangular and hexagonal mesophases. These results show that, for these complexes, the ratio of the volume of the rigid core to the volume filled by the flexible chains determines the symmetry of the resulting columnar mesophase.

E. d^8 ELECTRONIC CONFIGURATION

Configuration d^8 leads most commonly to a 4-coordinate square-planar stereochemistry (see, for example, ref. 40). For this reason, ions of this configuration have been widely used in the synthesis of mesogenic complexes, which, as already pointed out, require anisotropic geometries. Mesogenic complexes have been reported for Fe(0), Rh(I), Ir(I), Ni(II), Pd(II), Pt(II) and Au(III) with a clear predominance of studies on Ni(II) and Pd(II).

(i) Iron(0) complexes

In spite of their non-planar geometry about the metallic atom, the butadiene tricarbonyl complexes represented in Fig. 13 show mesogenic properties when rod-like substituents are present in X or Y [41]. The mesogenic compounds reported show N or/and S_A mesophases in temperature ranges strongly dependent on the nature of the substituents. The metallic centre of these complexes is chiral when X and Y are different, and the enantiomers are easily accessible [42]. This characteristic,

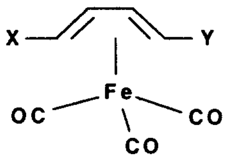


Fig. 13.

together with the strong dipole moment of the (diene)Fe group [43], make these complexes very suitable as dopants in ferroelectric liquid crystal devices.

(ii) Rhodium(I) complexes

The *cis*-dicarbonyl complexes represented in Fig. 14 are the only reported mesogenic Rh(I) complexes.

The 4-alkyloxy-4′-cyanobiphenyl complexes [44] can be prepared by bridge splitting reaction between the ligand and the dimeric complex $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$. The 4-pyridylmethylene-4′-alkyloxyaniline [45] and 4-alkyloxy-4′-stilbazole [46] derivatives are most conveniently obtained by reaction of $[Rh_2(\mu\text{-}Cl)_2(cod)_2]$ (cod = cycloocta-1,5-diene) with the corresponding pyridine ligand, followed by bubbling of CO.

The $n=9$ nitrile complex shows a range of 1°C of nematic mesophase, whereas the $n=10$ derivative shows a monotropic smectic mesophase. The iminopyridine derivatives give S_A mesophases for $n \geqslant 9$ and nematic for $n=8$. Interestingly, the coordination of the non-mesogenic 4-pyridylmethylene-4′-alkyloxyaniline ligands gives rise to better mesogenic properties than those obtained by coordination of the liquid crystalline alkyloxycyanobiphenyls. Stilbazole derivatives also display nematic ($n=4$–8) and S_A ($n=7$–12) mesophases, showing mesogenic ranges somewhat greater than those observed for the iminopyridine complexes.

Derivatives containing 4-pyridylmethylene-4′-alkyloxyanilines and different auxiliary ligands have been also synthesized [45]. Complexes of formula $[RhCl(CO)(NC_5H_4{-}4\text{-}CH{=}N{-}C_6H_4{-}4'\text{-}OC_nH_{2n+1})(P(OMe)_3)]$ have lower melting points than their dicarbonyl analogues; however, the bigger size of the $P(OMe)_3$ group in relation to carbonyl prevents regular ordering on melting, and so the complexes do not exhibit mesogenic behaviour. Similarly, the diolefinic complexes $[RhCl(cod)(NC_5H_4{-}4\text{-}CH{=}N{-}C_6H_4{-}4'\text{-}OC_nH_{2n+1})]$ do not exhibit mesogenic properties. The complexes *trans*-$[RhCl(CO)(NC_5H_4{-}4\text{-}CH{=}N{-}C_6H_4{-}4'\text{-}OC_nH_{2n+1})_2]$ (Fig. 15) despite their rod-like shape do not show mesogenic properties. In fact, these compounds exhibit very high melting points (decomposition above

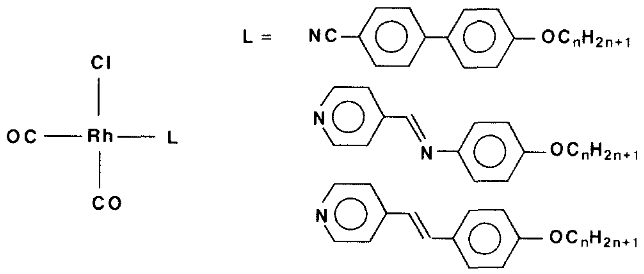


Fig. 14.

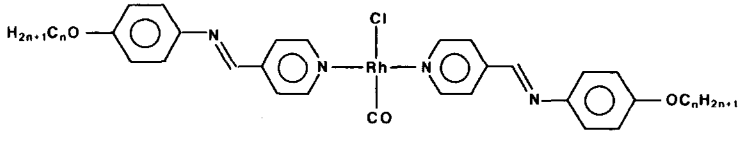


Fig. 15.

300°C). These observations suggest that there are strong intermolecular interactions in the solid due to a favourable molecular geometry, and as a result, mesophases cannot be observed. Replacement of the chloride ligand by an acetate or a trifluoroacetate, as in the complexes $[Rh(OCOCR_3)(CO)_2(NC_5H_4\text{-}4\text{-}CH{=}N\text{-}C_6H_4\text{-}4'\text{-}OC_nH_{2n+1})]$ (R = H, F), leads to non-mesogenic compounds. These mononuclear derivatives undergo intermolecualr reaction in dichloromethane solution to give square-planar tetranuclear clusters of formula $[Rh_4(\mu\text{-}OCOCR_3)_4(\mu\text{-}CO)_4(NC_5H_4\text{-}4\text{-}CH{=}N\text{-}C_6H_4\text{-}4'\text{-}OC_nH_{2n+1})_4]$ (R = H, F) [47]. The structure of the R = H, $n = 14$ derivative is shown in Fig. 16. This complex shows an endothermic transition at 99°C between the crystalline phase and a viscous fluid phase [48] which is stable up to 220°C, a temperature at which the cluster decomposes. If confirmed, this would be the first liquid crystalline cluster.

(iii) Iridium(I) complexes

The iridium complexes $[IrCl(CO)_2(NC_5H_4\text{-}4\text{-}CH{=}N\text{-}C_6H_4\text{-}4'\text{-}OC_nH_{2n+1})]$ provided the first examples of liquid crystals obtained by coordination of a metallic

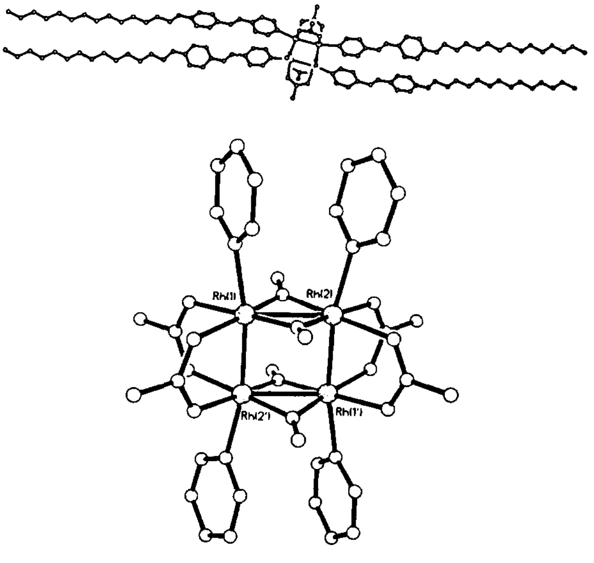


Fig. 16. Top, structure of the cluster $[Rh_4(\mu\text{-}O_2CCH_3)_4(\mu\text{-}CO)_4(NC_5H_4\text{-}4\text{-}CH{=}N\text{-}C_6H_4\text{-}4'\text{-}OC_{14}H_{29})_4]$. Below, detail of the tetranuclear core of the cluster.

fragment to a single molecule of a non-mesogenic ligand, opening up new prospects in the synthesis of mesogenic molecules [49]. They can be prepared by reaction between the 4-pyridylmethylene-4′-alkyloxyaniline ligand and $[Ir_2(\mu\text{-}Cl)_2(cod)_2]$ followed by CO displacement of the coordinated diene. The mesogenic behaviour of these compounds is similar to that shown by their Rh(I) analogues, exhibiting nematic and S_A mesophases, although Ir(I) complexes show better thermal stability. Isostructural complexes containing 4-alkyloxy-4′-stilbazoles as ligands display rather similar mesogenic properties [46]. Optical measurements carried out on the latter show that these materials present high birefringences [50].

(iv) Nickel(II) complexes

(a) Complexes with sulphur donor ligands

The synthetic procedure shown in the equation

$$\mathrm{RBr} \xrightarrow[(2)\,CS_2]{(1)\,Mg} \mathrm{RCSSH} \xrightarrow[EtOH]{NiCl_2\cdot 6H_2O} [Ni_2(S_2CR)_4] \qquad (1)$$

in which $R=C_nH_{2n+1}$ leads to Ni(II) dinuclear complexes with alkyldithiocarboxylates as ligands [51].

Figure 17 shows the X-ray crystal structure of the $R=CH_3$ complex [52]. A similar dinuclear arrangement is found in the $R=CH_2{-}C_6H_5$ derivative [53]. Each nickel atom has five neighbours, i.e. four sulphur atoms and a nickel atom, in a tetragonally distorted square-pyramidal geometry. The Ni–Ni distance (2.564(1) Å) is slightly too long to be considered a bonding distance. Each nickel atom shows an “inward” displacement of 0.11 Å from the S_4 plane in the direction of the other nickel atom. The two NiS_4 squares are twisted 24° from the eclipsed geometry, in contrast to other similar compounds which show eclipsed conformations [34,54].

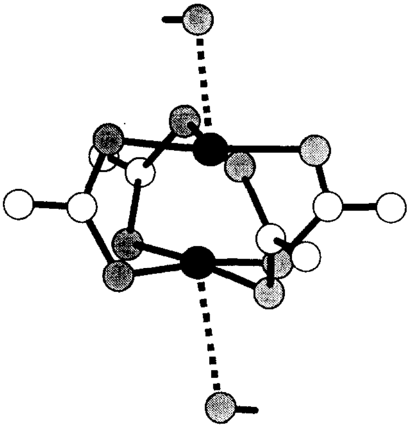


Fig. 17. Structure of $[Ni_2(\mu\text{-}S_2CCH_3)_4]$. Adapted from ref. 52.

The dimeric units are in the "slipped stack" arrangement so that there is a Ni–S contact between two adjacent molecules.

The complexes with $n=5$–12 exhibit a monotropic mesophase which gives an X-ray diffraction powder pattern characteristic of a lamellar structure [55], in contrast to the columnar mesophase (D_{ho}) found in alkanoate complexes with similar structures. Attempts to characterize this lamellar phase completely have failed due to decomposition of the complexes.

The synthetic route of eqn. (1) leads to bis-chelate complexes when 4-alkyloxydithiobenzoates ($^{-}S_2C$–C_6H_4–4-OC_nH_{2n+1}) are used as ligands [56].

These complexes are described as square-planar Ni(II) derivatives on the basis of their electronic spectra in chloroform, which are similar to those obtained for bis(dithiobenzoate)nickel(II) [57]. The latter is trinuclear in the solid state, as shown in Fig. 18. The structure shows two types of nickel atom, essentially square-planar but distorted because of the existence of Ni–S bridging interactions (2.776(5) and 3.108(5) Å).

Complexes with $n=4$, 8 exhibit two enantiotropic lamellar mesophases assigned as S_H and S_C on the basis of their microscopic textures and X-ray powder diagrams [58]. These mesophases can be reproduced on several heating and cooling cycles provided that a clearing temperature is not reached. Figure 19 shows the DSC thermogram of the $n=8$ complex. Red isotropic liquids are obtained when the compounds are heated above their clearing points. On cooling, these red liquids produce nematic mesophases which are the only ones present in subsequent heating and cooling cycles. This behaviour has been attributed to the intermolecular process shown in Scheme 3 [59]. The IR, NMR and electronic spectra confirm the formation of (dithiobenzoate)(perthiobenzoate)nickel(II) complexes. Figure 20 shows the X-ray crystal structure of [$Ni(S_3CC_6H_4$–4-$^{i}Pr)(S_2CC_6H_4$–4-$^{i}Pr)$] [60], illustrating the planar angular shape of these mixed-ligand complexes.

The $n=4$ and $n=8$ mixed-ligand derivatives show ranges of 100 and 80°C of nematic mesophase, respectively. Additionally, the complexes exhibit two crystalline phases related by "double melting behaviour" via the nematic phase. The "double-

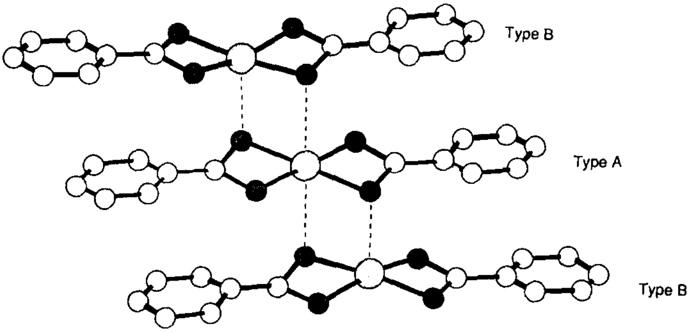


Fig. 18. Structure of [$Ni(S_2C$–$C_6H_5)_2$]. Adapted from ref. 57.

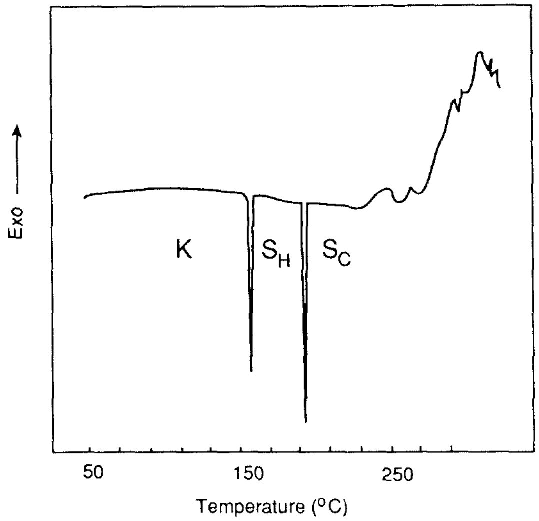
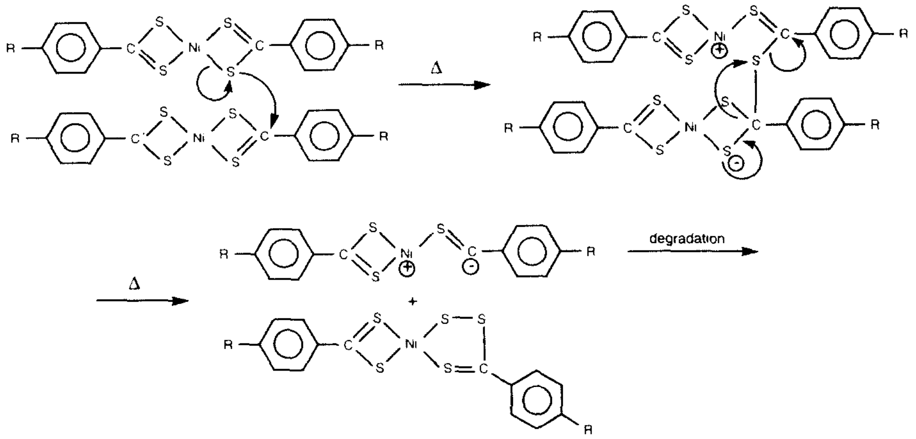


Fig. 19. DSC thermogram of the first heating process of the complex $[Ni_2(S_2C{-}C_6H_4{-}4{-}OC_8H_{15})_2]$. Adapted from ref. 58.



Scheme 3. Intermolecular rearrangement proposed in $[Ni(S_2C{-}4{-}R{-}C_6H_5)_2]$ complexes to explain their thermal behaviour.

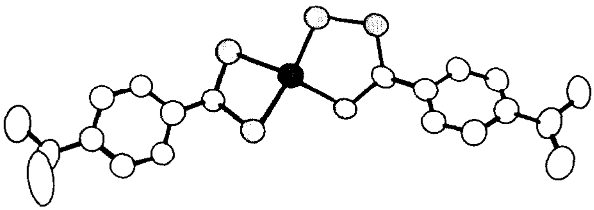
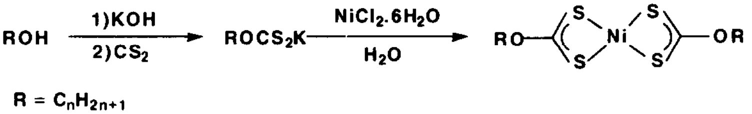


Fig. 20. Structure of $[Ni(S_3C{-}C_6H_4{-}4{-}{}^iPr)(S_2C{-}C_6H_4{-}4{-}{}^iPr)]$. Adapted from ref. 60.

melting behaviour" phenomenon, which has been extensively studied by Ohta et al. [61,62], is a kinetic effect based on the existence of a metastable crystal phase which melts at a lower temperature than the thermodynamically stable crystal phase. Figure 21 shows two DSC thermograms of the mixed-ligand complex ($n = 4$) at different heating rates, along with a qualitative free energy vs. temperature diagram which illustrates this phenomenon.

For sufficiently fast heating rates (Fig. 21(a)), the room-temperature-stable crystal phase (K_1) can exist at temperatures above the K_1–K_2 transition temperature due to the slow kinetics of the crystal–crystal phase transitions. Thus, K_1 melts directly to the nematic phase* (T_{m1}) giving rise to an endothermic peak (I). Immediately, the nematic phase transforms into phase K_2, which is thermodynamically stable at this temperature (exothermic peak II). The following peaks of the DSC (endothermic peaks III and IV) correspond to the K_2–N and N–I transitions respectively. At slow heating rates (Fig. 21(b)), the DSC obtained corresponds to the thermodynamically favoured path and no "double melting behaviour" is observed.

Mesogenic mononuclear complexes containing xanthates as ligands can be prepared following the route [63]



(2)

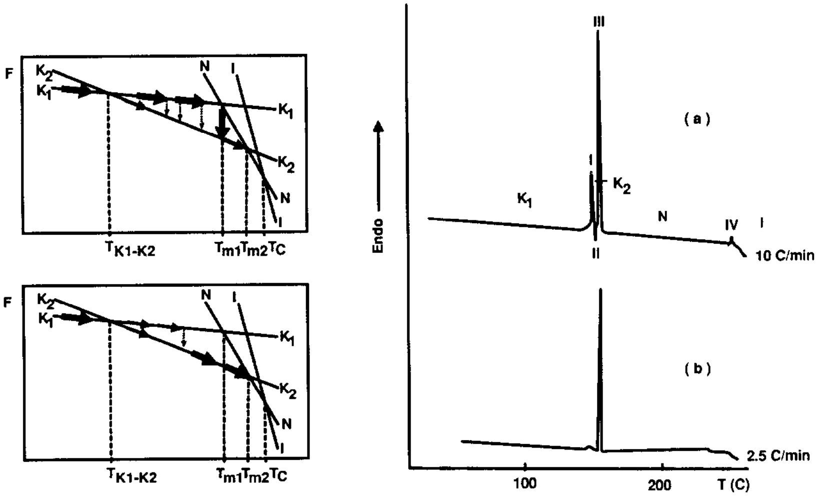


Fig. 21. Right, DSC thermograms of the heating process of the complex $[Ni(S_3C{-}C_6H_4{-}4{-}OC_4H_9)(S_2C{-}C_6H_4{-}4{-}OC_4H_9)]$ at different scan rates. Left, qualitative free energy vs. temperature diagrams illustrating the thermodynamic pathway that begins each DSC thermogram. Adapted from ref. 58.

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* Or the isotropic liquid for non-mesogenic materials.

Derivatives with alkyloxy chains longer than 12 carbon atoms display very short mesogenic ranges (approx. 1°C). The mesophase has been identified as an ordered smectic phase (S_E, S_G or S_H) [55]. Complexes with odd number of carbons in their chains display double melting behaviour.

The bisdithiolene complexes $[Ni(S_2C_2H{-}C_6H_4{-}4{-}C_nH_{2n+1})_2]$** also exhibit mesogenic properties. The nickel atom has a square-planar stereochemistry as can be seen in the crystal structure of the $n=8$ complex [65] (Fig. 22). Complexes with $n=4$, 5 display nematic mesomorphism whereas complexes with $n \geqslant 6$ give S_C mesophases [66], which is to be expected from the molecular arrangement shown in the crystalline phase.

The dithiolene complex shown in Fig. 23 forms a disordered hexagonal columnar mesophase (D_{hd}) which has been characterized by X-ray diffraction [67].

Although some other dithiolene nickel complexes have been synthesized and mesophases have been reported in such systems [68], later X-ray diffraction experiments have shown that these phases should be considered crystals rather than mesophases [69].

(b) Complexes with Schiff's base imines

The complexes represented in Fig. 24 can be obtained by reaction of the corresponding Schiff's base with nickel(II) acetate under refluxing ethanol [70]. The

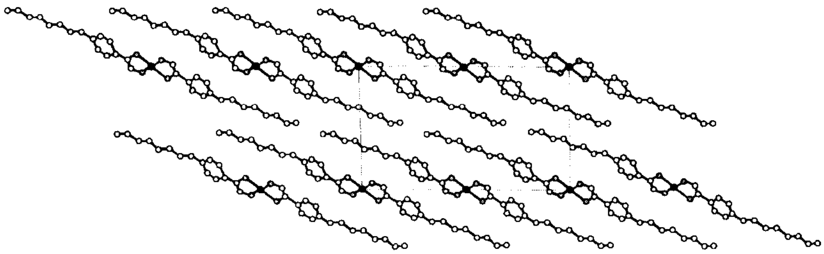


Fig. 22. Structure and molecular packing of $[Ni(S_2C_2{-}C_6H_4{-}4{-}C_8H_{17})_2]$. Adapted from ref. 65.

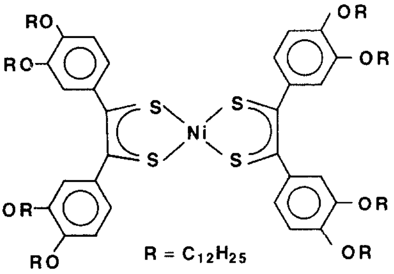


Fig. 23.

** These compounds have been included as Ni(II) complexes, even though the assignment of an oxidation state for the metal is not evident, due to the special nature of the dithiolene ligands [64].

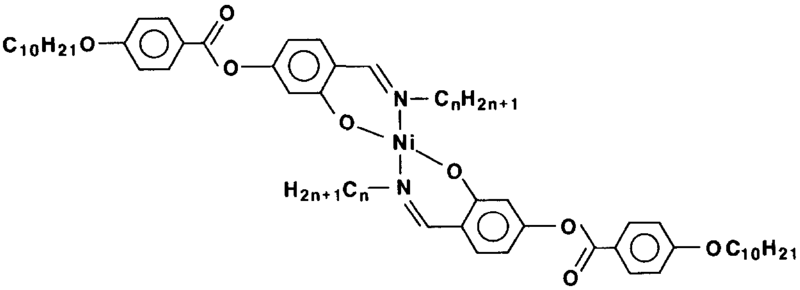


Fig. 24.

nickel is square-planar coordinated as can be inferred from the diamagnetic nature of the complexes and according to the common stereochemistry of this kind of compound [71]. Complexes with $n = 1, 2$ display monotropic nematic mesomorphism whereas for $n \geqslant 3$ the nematic mesophases are enantiotropic.

Complexes with tetradentate Schiff's bases as ligands (Fig. 25) give smectic mesomorphism. These materials have been prepared by two different teams following alternative synthetic procedures [72,73]. Even though both reports agree about the formation of smectic mesophases, the thermodynamic data reported show large differences.

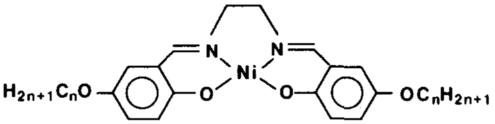
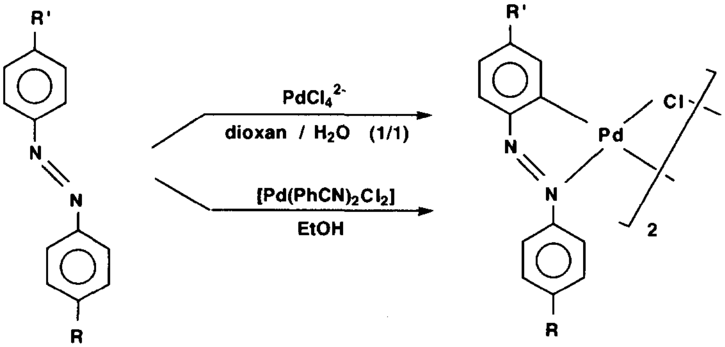


Fig. 25.

(v) Palladium(II) complexes

(a) Complexes with orthometallated ligands

Orthometallated complexes are by far the most widely studied mesogenic palladium(II) complexes. Dinuclear Cl-bridged complexes can be prepared by orthometallation of substituted azobenzenes, according to eqn. (3) [74,75].



(3)

The formation of the more symmetric trans isomer is favoured. In non-symmetric azobenzenes ($R \neq R'$), the metallation occurs preferentially at the most electron-rich ring [76]. As a consequence, some products of these reactions have been considered as unique isomers [77], but the NMR spectra of most of such materials show that they would be better regarded as mixtures of isomers arising from competitive metallation of both rings [78,79].

Figure 26 shows the crystal structure of the non-mesogenic complex (8-hydroxyquinolinato)[2-(4′-methoxyphenylazo-N^2)-5-methoxyphenyl]palladium(II) [80]. The azobenzene ligand adopts a non-planar conformation in which the uncoordinated methoxyphenyl portion is rotated 109° with respect to the Pd coordination plane. In spite of the differences between this mononuclear derivative and the mesogenic dimeric complexes, a similar ligand conformation can be assumed in both systems, but this does not necessarily mean that this rotated conformation is maintained in the mesophase.

The azobenzene ligands with $R = OC_nH_{2n+1}$ and $R' = H$ are not mesogenic, whereas their dimeric Cl-bridged Pd(II) complexes display S_A monotropic mesophases for $n \geqslant 10$ [79,81]. When using mesogenic azobenzene ligands, complexation widens the temperature range of mesogenic behaviour and increases the melting points. Thus, complexes with $R = OC_nH_{2n+1}$ give nematic mesophases when $R' = C_nH_{2n+1}$ [78], whereas complexes with $R' = O_2C{-}C_nH_{2n+1}$ display, in addition to the nematic mesophase, S_A and S_B monotropic phases [77,81]. The nematic phases shown by these complexes are biaxial, as has been demonstrated by conoscopic observations [82].

Reaction of Cl-bridged compounds with other halides (Br^-, I^-) yields metathetical complexes which show nematic and smectic mesophases and higher melting and clearing temperatures [81,83]. The Cl-bridged complexes undergo bridge-splitting reactions when treated with pyridine or quinoline, yielding mononuclear complexes which exhibit both nematic and smectic phases (S_A for pyridine and S_B for quinoline), whereas the corresponding aniline or triphenylphosphine complexes are not meso-

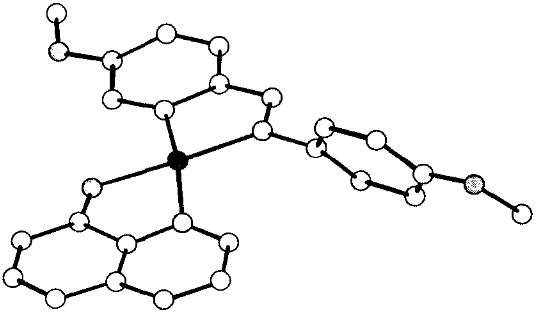
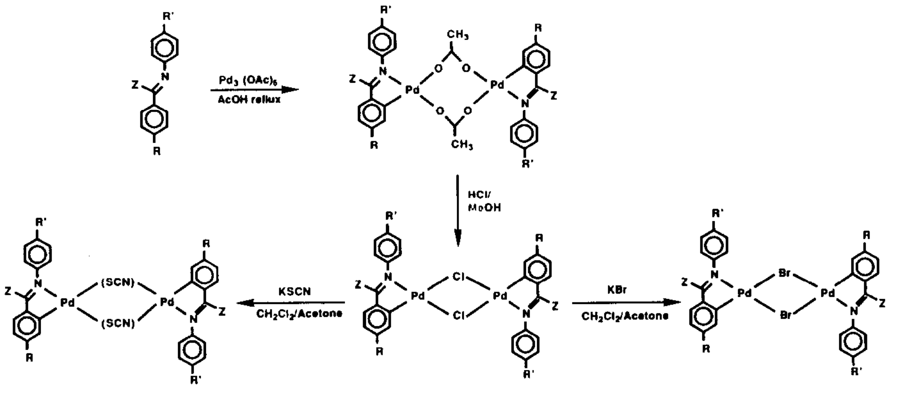


Fig. 26. Structure of $[Pd(5\text{-}CH_3O{-}C_6H_3{-}2\text{-}(N{=}N{-}C_6H_4{-}4'\text{-}OCH_3))\text{-}(OC_9H_6N)]$. Adapted from ref. 80.

genic. Spectroscopic data suggest that the incoming ligand coordinates trans to the orthometallated carbon atom [83].

Dinuclear Pd(II) complexes similar to those already described can be obtained by using Schiff's base imines as ligands. Scheme 4 illustrates the synthesis of several derivatives with different bridging ligands [84]. Structural studies [85] demonstrate that only trans isomers are formed. The NMR spectra lead to the conclusion that, at least in solution, the complexes with halogen and thiocyanate bridges are planar, whereas the acetato-bridged complexes are not planar. The thiocyanate complexes however, are obtained as a mixture of isomers which arise from the relative disposition of the asymmetrical bridging ligands. Figure 27(a) represents the crystal structure of the mesogenic complex $[Pd_2(5\text{-}CH_3O\text{–}C_6H_3\text{–}2\text{-}(CH{=}N\text{–}C_6H_4\text{–}4'\text{-}C_4H_9))_2(\mu\text{-}Cl)_2]$ [86], showing again a non-planar conformation for the orthometallated ligand. On the other hand, the crystal structure of the non-mesogenic complex $[Pd_2(3\text{-}CH_3O\text{–}C_6H_3\text{–}2\text{-}CH{=}N\text{–}C_6H_{13})_2(\mu\text{-}O_2CCH_3)_2]$ [87] (Fig. 27(b)) illustrates the



Scheme 4. Synthetic routes for obtaining imine ortho-palladated derivatives with different bridging ligands.

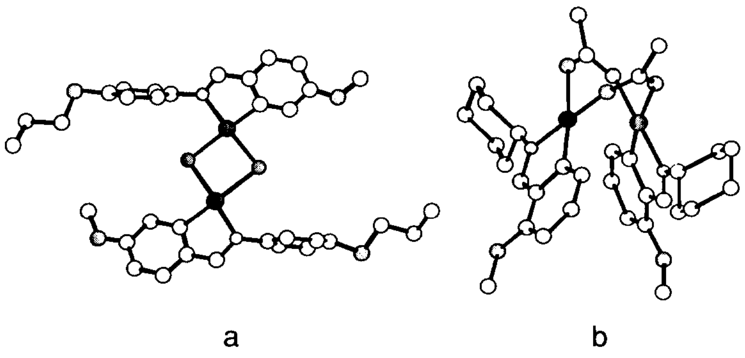


Fig. 27. (a) Structure of $[Pd_2(5\text{-}CH_3O\text{–}C_6H_3\text{–}2\text{-}(CH{=}N\text{–}C_6H_4\text{–}4'\text{-}C_4H_9))_2(\mu\text{-}Cl)_2]$, adapted from ref. 86. (b) Structure of $[Pd_2(3\text{-}CH_3O\text{–}C_6H_3\text{–}2\text{-}(CH{=}N\text{–}C_6H_{13}))_2(\mu\text{-}O_2CCH_3)_2]$. Adapted from ref. 87.

characteristic rigid roof-shaped geometry of the acetate-bridged complexes, in which the coordination planes of each palladium form very closed dihedral angles.

The mesogenic behaviour of derivatives with $R=OC_{10}H_{21}$, $R'=OC_{10}H_{21}$, $C_{10}H_{21}$ and $Z=H$, CH_3 has been studied [84]. The Cl-bridged complexes with $Z=H$ display S_A and S_C mesophases, whereas only S_A phases are obtained for $Z=CH_3$. The other halogen-bridged compounds, as well as the thiocyanate-bridged dimers, show N or S_A mesomorphism, depending on the chain length. The mesogenic properties of the acetato-bridged complexes are rather poor, and so the only mesogenic derivative ($R'=C_{10}H_{21}$ and $Z=H$) exhibits a monotropic S_A phase. The halogen-bridged derivatives are the ones showing the lowest melting points amongst this family of complexes. Chlorine-bridged complexes with different polar groups in the R and R′ positions have been prepared in order to study the influence of such substituents on the liquid crystal properties [88,89]. The results show that the central core is mainly responsible for the liquid crystal properties, whereas the position of the polar group does not play an important role. However, the nature of the anilinic substituent has significant influence on the mesogenic properties.

Treatment of the Cl-bridged complexes with Tl(acac) leads to the mesogenic mononuclear compounds represented in Fig. 28. These complexes show lower melting points and less ordered mesophases (N and S_A) than their parent dinuclear species. This effect must be related to the less symmetrical shape of the mononuclear compounds [90].

Azomethyne ligands derived from 2,3,4-trialkyloxybenzaldehyde also lead to mesogenic ortho-palladated complexes. Both types of complex shown in Fig. 29 display nematic discotic (N_D) liquid crystalline phases [91].

Another family of ligands that give orthopalladated mesogenic dimers are those represented in Fig. 30. Mono-orthopalladation of these azines is carried out by refluxing mixtures of $[Pd_3(O_2CCH_3)_6]$ and the corresponding azine in anhydrous acetic acid, yielding acetato-bridged complexes [92]. Halogen-bridged compounds can be easily obtained by metathetical reaction of these acetate complexes with the corresponding alkaline halide. The NMR spectra show that, for halogen-bridged

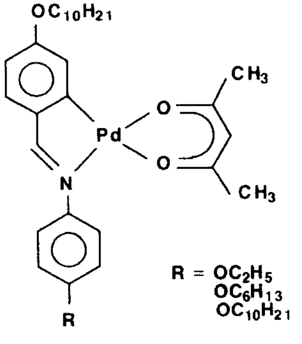
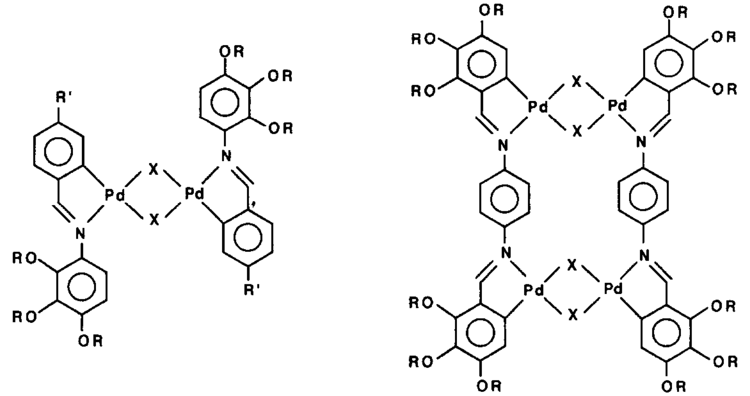


Fig. 28.



$R, R' = C_6H_{13}$, $R = C_6H_{13}$, $R' = OC_6H_{13}$
X = OAc, Cl, Br, SCN

$R = C_nH_{2n+1}$
X= OAc, Cl, Br, SCN

Fig. 29.

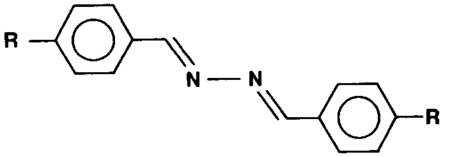


Fig. 30.

complexes, only the trans isomer is formed, whereas cis and trans isomers are detected in the spectra of thiocyanato-bridged derivatives (cis/trans = 3/2). The acetate complexes are also obtained as a mixture of isomers (75% trans), regardless of the synthesis procedure employed [93]. All the complexes prepared with $R = OC_{10}H_{21}$ are mesogenic, showing enantiotropic S_C mesophases. The appearance of an enantiotropic mesophase for the acetato-bridged complex is noticeable, since this bridging group has proved to diminish mesogenic behaviour in the imine derivatives already described. Two factors may contribute to this improvement of mesogenic behaviour: the extra C=N link in the azines and the existence of a mixture of cis and trans isomers.

These acetato-bridged complexes have received special attention due to their peculiar structure. A family of complexes with carboxylate bridges of varying lengths has been prepared [94] by treatment of the chloro-bridged complex $[Pd_2(5\text{-}C_{10}H_{21}O\text{–}C_6H_3\text{–}2\text{-}(CH{=}N\text{–}N{=}CH\text{–}C_6H_4\text{–}4'\text{-}OC_{10}H_{21}))_2(\mu\text{-}Cl)_2]$ with an excess of the corresponding $NaO_2C\text{–}C_nH_{2n+1}$ salt. The resulting complexes (again mixtures of cis and trans isomers) display the mesogenic behaviour shown in Fig. 31. It is remarkable that, in contrast to what happens in typical rod-like molecules where the smectic phases are suppressed by lateral branches, these complexes show smectic

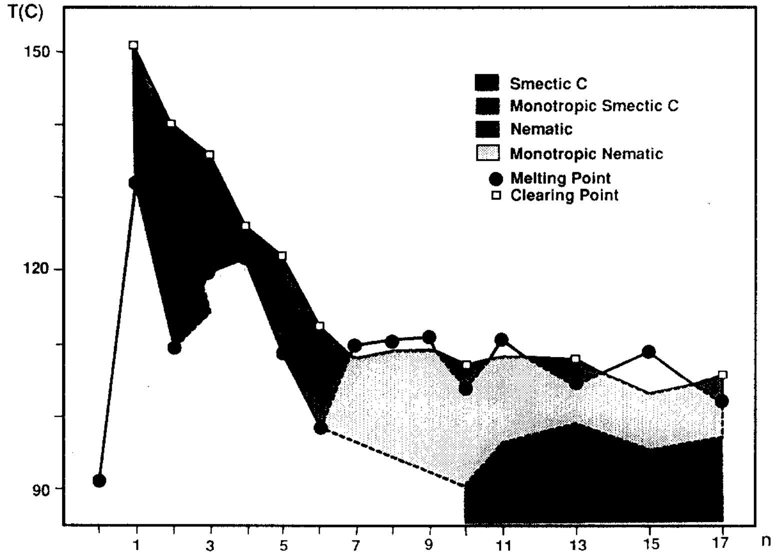


Fig. 31. Transition temperatures as a function of the bridging carboxylate length of the complexes [Pd_2(5-$C_{10}H_{21}O$–C_6H_3–2-(CH=N–N=CH–C_6H_4–4′-$OC_{10}H_{21}$))$_2$(μ-O_2C–C_nH_{2n+1})$_2$]. Adapted from ref. 94.

phases for the shortest ($n = 1$–3) and for the longest chains ($n \geqslant 10$) but not for the intermediate lengths. Furthermore, carboxylates of intermediate length produce a pronounced decrease in the N–I transition temperatures. In other words, small increases in the length of the carboxylate chain make the molecular ordering in the mesophase more difficult, whereas sufficiently long carboxylates again facilitate this molecular arrangement. This behaviour can be easily understood by the intuitive model shown in Fig. 32. The identity of these N and S_C mesophases has been confirmed by X-ray diffraction experiments on magnetically aligned samples.

Rigid roof-shaped trans complexes are chiral, and since formation of these

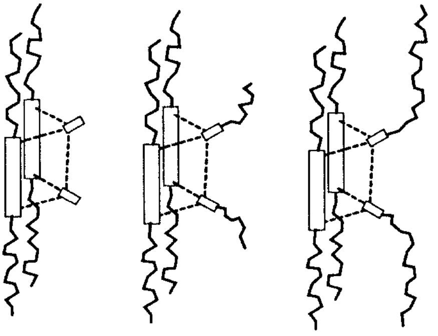


Fig. 32. Model for the carboxylate chain arrangement in the complexes [Pd_2(5-$C_{10}H_{21}O$–C_6H_3–2-(CH=N–N=CH–C_6H_4–4′-$OC_{10}H_{21}$))$_2$(μ-O_2C–C_nH_{2n+1})$_2$]. Adapted from ref. 94.

carboxylato-bridged complexes is not enantioselective, the trans isomer must be a mixture of the two enantiomers. Additionally, these complexes display S_C mesophases, and therefore, after introduction of chirality, they can give rise to ferroelectric liquid crystal properties [95]. Chirality can easily be introduced by using optical active carboxylates as bridging ligands, which convert the trans enantiomers in two diastereomers. Thus, dimeric complexes containing these azine ligands and (R)–$CHCl(Me)CO_2$ bridges consist of a mixture of *trans*-ΛR,R (34%), *trans*-ΔR,R (34%) and *cis*-R,R (32%) diastereomers, all of them optically active. These mixtures display S_C chiral mesophases that show ferroelectric liquid crystal behaviour [96]. A preliminary study of their physical properties showed that the materials responded to applied electric fields (switching behaviour). However, their electro-optical responses are slower than those of calamitic S_C^* phases due to the high viscosity of the material.

Very recently, Ghedini et al. have described the synthesis and mesogenic behaviour of dinuclear complexes with orthometallated 5-alkyl-2(4'-alkyloxyphenyl)pyrimidine ligands and several bridging groups [97]. Again, the planar halogen-bridged complexes show mesomorphism (smectic), whereas the non-planar acetato-bridged complexes do not. Reaction of the Cl-bridged complexes with $AgBF_4$ followed by addition of 2,2'-bipyridine yields cationic complexes which show nematic mesomorphism. Similar complexes containing phenanthroline are not mesogenic. Neutral mononuclear compounds can be obtained by using anionic chelating ligands such as 8-hydroxyquinolinate or β-diketonates. The former leads to non-mesogenic complexes, whereas β-diketonate derivatives display monotropic S_A mesophases [98].

(b) Complexes with other ligands

Treatment of basic solutions of *N*-(4'-alkyloxyphenyl)-4-(alkyloxy)salicylaldimines with *trans*-$PdCl_2(C_6H_4CN)_2$ yield complexes in which palladium(II) is coordinated to two salicylaldiminate ligands [99]. The X-ray crystal structure of one of them is shown in Fig. 33 [100]. These complexes display S_C and S_A mesophases at temperatures about 200°C [99]. The mesophases have been characterized by X-ray diffraction. The results show a layer thickness for the S_A mesophase similar to the molecular length, in agreement with monomolecular smectic layers.

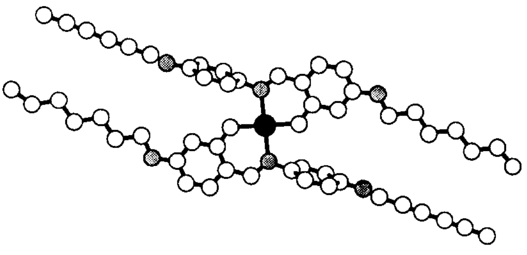


Fig. 33. Structure of [$\overline{Pd(5\text{-}C_7H_{15}O{-}C_6H_3(O})$–2-(C=N–$C_6H_4$–4'-$OC_6H_{13}$))$_2$]. Adapted from ref. 100.

The reaction of *trans*-$PdCl_2(C_6H_4CN)_2$ with mesogenic nitriles (L) yields the mesogenic complexes *trans*-$PdCl_2(L)_2$ [101]. The X-ray crystal structure of the compound with L = 4-pentyl-4′-cyanobiphenyl is shown in Fig. 34[44,102]. Complexes with 4-alkylcyanobiphenyl or 4-alkylcyanobicyclohexyl (L) ligands exhibit monotropic nematic mesomorphism, whereas L = 4-alkyloxycyanobiphenyl derivatives show enantiotropic S_A and S_C mesophases for $n \geqslant 10$, and nematic phases for shorter terminal chains.

Similar complexes with 4-alkyloxy-4′-stilbazoles can also be obtained by ligand exchange from *trans*-$PdCl_2(C_6H_4CN)_2$. These complexes show high-temperature smectic phases for $n \geqslant 12$. Replacement of Cl by hexanoate ligands gives complexes which show nematic phases for $n \geqslant 8$ at noticeably lower temperatures [103].

Dithiobenzoate complexes similar to those already mentioned for Ni(II) can also be obtained for Pd(II). Figure 35 shows the crystal structure of $[Pd(S_2CC_6H_4{-}4{-}OC_8H_{17})_2]$ [102] where the mononuclear units are weakly associated forming dimers (Pd–S intermolecular ⩾3.38 Å). This complex exhibits two non-identified smectic mesophases along with a nematic phase, and decomposes as its cleaning temperature.

A family of mesogenic β-diketonate palladium(II) derivatives were reported in 1977, although their mesogenic properties have not yet been characterized [104].

(vi) Platinum(II) complexes

The bis-alkynyl Pt(II) complexes shown in Fig. 36 can be obtained by successive substitution of the chloride ligands by terminal alkynes in the presence of CuCl and diethylamine [105].

The complexes show nematic mesophases above 170°C. When both alkyloxy terminal chains are longer than 10 carbon atoms, an S_A mesophase is present below the nematic mesophase. The stabilization of thermotropic mesophases in the presence of tertiary phosphine ligands is noticeable, since these ligands confer great stability

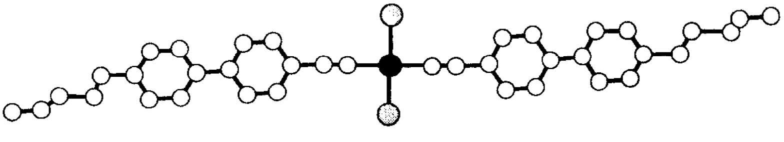


Fig. 34. Structure of *trans*-$[PdCl_2(NC{-}C_6H_4{-}C_6H_4{-}4{-}C_5H_{11})_2]$. Adapted from ref. 44.

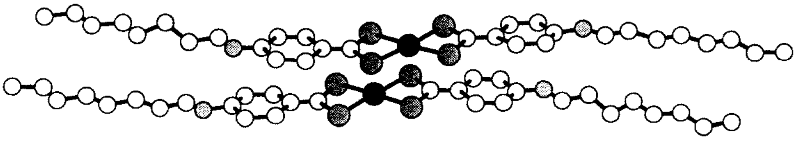


Fig. 35. Structure of $[Pd(S_2C{-}C_6H_4{-}4{-}OC_8H_{17})_2]$. Adapted from ref. 102.

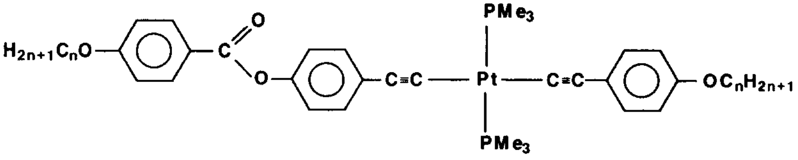


Fig. 36.

to the metallorganic complexes. Polymers based on units similar to these complexes form lyotropic nematic mesophases in trichloroethylene solution [106].

Complexes of formula *trans*-$PtCl_2L(C_2H_4)_2$ are formed in high yields from Zeise's salt by reaction with 4-alkyloxy-4′-stilbazoles (L). Replacement of ethene by other α-olefins yields the derivatives represented in Fig. 37 [103]. A systematic study of the influence of n and m shows that the molecules are not mesogenic for shorter chains ($m+n \leqslant 7$), whereas for long chain derivatives ($n+m \geqslant 12$), enantiotropic S_A mesophases are observed. Monotropic S_A mesomorphism is found for complexes which lay in the band between the non-mesogenic and enantiotropic regions. The low melting points obtained support the idea that less symmetric complexes lead to lower temperature mesogens.

Mesogenic cyanobiphenyl Pt(II) complexes can be obtained by a procedure similar to that already described for their Pd(II) analogues [44,101], or alternatively by direct reaction between the cyanobiphenyl ligands and $[PtCl_2]_n$ [102]. Figure 38 shows the X-ray crystal structure of *trans*-dichlorobis(4-octyl-4′-cyanobiphenyl)platinum(II) [44]. In spite of the structural analogy between the Pd and Pt derivatives, their mesogenic properties are different. Thus, while Pd complexes display monotropic nematic mesophases, enantiotropic N phases are found for Pt derivatives. The mesogenic behaviour of the 4-alkyloxy-4′-cyanobiphenyl complexes is also different for the Pd and the Pt compounds. In view of their structural similarities, these differences have been tentatively attributed to the greater reactivity of Pd(II) complexes in comparison with their Pt(II) analogues [44].

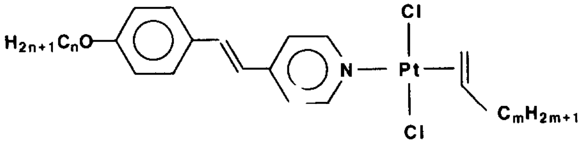


Fig. 37.

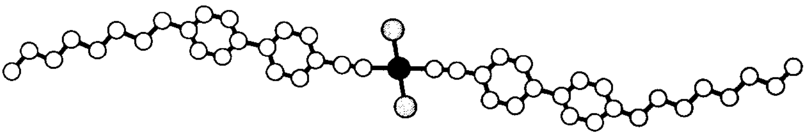


Fig. 38. Structure of *trans*-$[PtCl_2(NC{-}C_6H_4{-}C_6H_4{-}4{-}C_8H_{17})_2]$. Adapted from ref. 44.

The dithiolene complexes represented in Fig. 39 exhibit N and S_C mesomorphism, similar to that obtained for the Ni(II) analogous complexes [66]. Quite surprisingly, their Pd analogues do not show mesogenic properties. Again, the reason for this different behaviour is not understood, being attributed to structural differences between Pd and Pt derivatives. This explanation, however, is not supported by the fact that the X-ray structures of the bis(ethylene-1,2-dithiolene) complexes of Pd and Pt show that they are isostructural, both exhibiting M–M interactions (Pd–Pd = 2.79 Å, Pt–Pt 2.75 Å) [107].

(vii) Gold(III) complexes

The complexes shown in Fig. 40 are the only gold(III) mesogenic complexes hitherto reported. They display S_A mesophases in the range 150–200°C [102].

F. d^9 ELECTRONIC CONFIGURATION

(i) Copper(II) complexes

Copper(II) provides by far the most familiar and extensive chemistry for d^9 configuration. Its complexes are paramagnetic and this characteristic is, most likely, the reason for the extensive attention paid to Cu(II) liquid crystals. Most of the Cu(II) complexes show geometries derived from octahedral coordination, tetragonally distorted as a result of the Jahn–Teller effect [108]. The usual result is an elongation of the octahedron, giving a "4 + 2" coordination or, in the extreme case, a square-planar geometry.

(a) Complexes with β-diketonate ligands

The general synthetic procedure to obtain β-diketonato copper(II) complexes is shown in Scheme 5 [109–111]. Figure 41 shows the crystal structures of two mesogenic β-diketonato copper(II) complexes [112]. The copper atom is strictly square-planar in both molecules. However, the phenyl rings and also the terminal

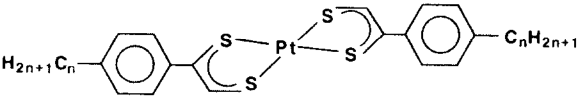


Fig. 39.

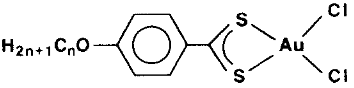
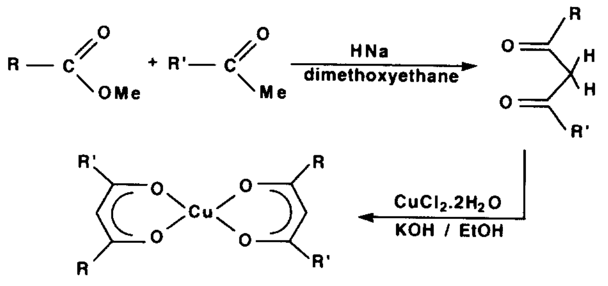


Fig. 40.



Scheme 5. General synthetic procedure for obtaining β-diketonato copper(II) complexes.

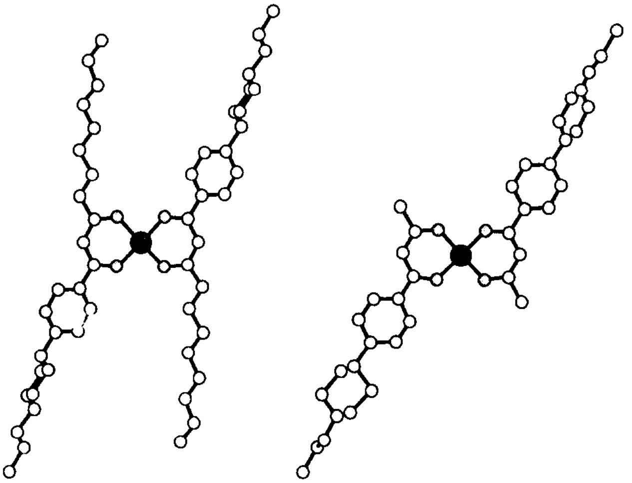


Fig. 41. Left, structure of $[Cu(C_8H_{17}CO{-}CH{-}CO{-}C_6H_4{-}4{-}C_6H_{10}{-}4'{-}(C_3H_7))_2]$ and right, $[Cu(CH_3{-}CO{-}CH{-}CO{-}C_6H_4{-}4{-}C_6H_{10}{-}4'{-}(C_3H_7))_2]$. Adapted from ref. 112.

chains are slightly tilted against the copper core, and therefore the molecules as a whole cannot be considered strictly planar. The molecules show a layer arrangement within the crystal, but no intermolecular contacts have been found.

Complexes containing eight alkyloxy chains, such as those represented in Fig. 42 ($R_1 = R_2 = OC_nH_{2n+1}$), exhibit a disordered hexagonal columnar mesophase [110,113], which has been identified by X-ray diffraction and miscibility experiments. The $n = 9$ and $n = 11$ derivatives show mesogenic ranges of 10 and 15°C, respectively, whereas for $n = 7$, the mesophase is monotropic. Ohta et al. have reported that some complexes of this series show double melting behaviour and double clearing behaviour [114]. In complexes where $R_1 \neq R_2$, mesogenic behaviour is found when $n = 9$, 9, 11, 11*, whereas the $n = 7$, 7, 11, 11 and $n = 3$, 3, 11, 11 derivatives are not mesomorphic. Changing the alkyloxy substituent from the 3,4 to the 3,5 phenyl ring

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* The nomenclature refers to the number of carbon atoms of the chains ordered R_1, R'_1, R_2, R'_2.

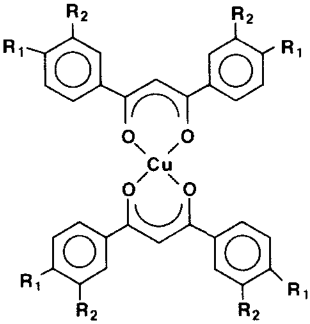

Fig. 42.

positions results in loss of the mesogenic behaviour. This could be caused by the steric interaction between chains which might bend the copper coordination plane. Substitution of the copper atom by nickel also destroys the liquid crystalline properties [110].

Complexes with only four paraffinic chains (Fig. 42; $R_2 = H$) also show discotic mesomorphism [109,115]. For alkyloxy chains ($R_1 = OC_nH_{2n+1}$) [116], the complexes display, besides a rich crystalline polymorphism, a mesophase whose clearing enthalpy is higher than that of fusion. This rare situation was first observed for the discotic mesophase of the 2,2′,6,6′-tetraarylbipiran-4-ylidenes [117] whose structure is rather similar to that of these β-diketonato-copper complexes. X-Ray diffraction diagrams* of this phase are characteristic of a lamellar mesophase, in which the disc-like molecules arrange in layers with their molecular plane tilted 5° from the direction perpendicular to the layer. This mesophase, known as D_L [118], is immiscible with tilted calamitic lamellar mesophases (as, for instance, S_C). Alkyl-chained ($R_1 = C_nH_{2n+1}$) complexes display mesogenic properties for $n \geq 4$ [119], even when the ligands employed are mesogenic only for $n \geq 7$. The mesophases exhibited are discotic, and for $n = 7$–9, each complex has plural discotic mesophases. None of these mesophases has been investigated by X-ray diffraction but some of the complexes have been studied by ESR [120]. The spectra obtained suggest the existence of a smectic phase of disc-like molecules (D_L), which additionally shows columnar correlations within the layers. The same conclusion is reached from an NMR study of the spin-lattice relaxation time of the chain protons [121]. Mixed-chained complexes ($R_1 = OC_nH_{2n+1}$, $R'_1 = C_nH_{2n+1}$) [122] show only one mesophase, identified as D_L by miscibility experiments. The temperature range in which this mesophase is stable is similar to that in which alkyl-chained complexes display several discotic phases.

The β-diketonato copper(II) complexes collected in Table 1 give rise to monotropic [111,112,123] or enantiotropic [124] paramagnetic nematic mesophases. Conoscopic observations on these compounds demonstrate the occurrence of a

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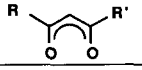
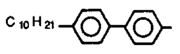
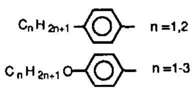
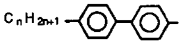
* The experiments were carried out on the supercooled mesophase at room temperature.

TABLE 1

β-Diketonato copper(II) complexes



R	R'	Ref
	 n =1,2 n =1-3	111, 123
 n = 3,5,7	C_nH_{2n+1} n =2,3,5-8	112
 n = 4, 8.	C_4H_9	124

biaxial nematic mesophase. Chandrasekhar et al. have suggested that these complexes incorporating the features of both disc-like and rod-like molecules are particularly convenient in obtaining biaxial nematic mesophases [125].

(b) Complexes with carboxylate ligands

Copper (II) alkanoates can be obtained by reaction of the sodium salt of the appropriate fatty acid with a solution of copper sulphate or acetate in ethanol [126,127]. The complexes are dinuclear, similar to those obtained for Cr(II), Mo(II) (Sect. B), Ru(II) (Sect. C.(ii)) and Rh(II) (Sect. D.(ii)) with the same ligands. Figure 43(a) shows the coordination sphere of the copper atom in copper(II) octanoate and decanoate [128]. Each copper atom is pseudo-octahedrally surrounded by six neighbours: the four oxygen atoms of the bridging carboxylate groups, the other copper atom of the dimer, and one axial oxygen atom belonging to an adjacent dimer. Thus, a specific feature of the crystalline structure is the existence of a polymeric lattice

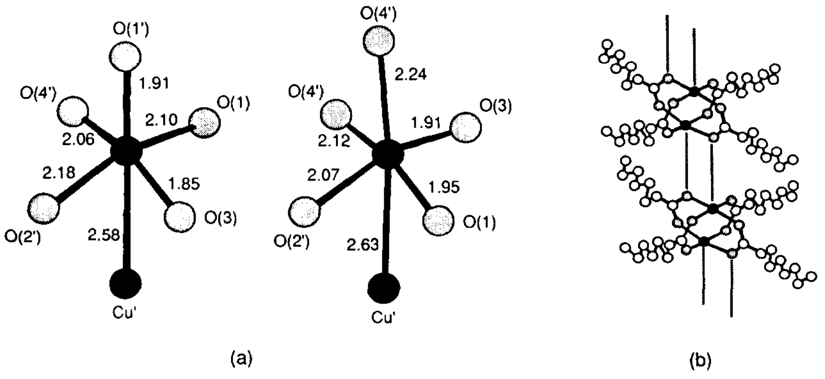


Fig. 43. (a) Coordination sphere of copper in copper(II) octanoate (left) and copper(II) decanoate (right). Adapted from ref. 128. (b) Representation of the solid state stacking of copper(II) alkanoates.

(Fig. 43(b)). All these alkanoate complexes $[Cu_2(O_2C{-}C_nH_{2n+1})_4]$, from butyrate ($n=3$) to lignocerate ($n=23$), exhibit a transition from a triclinic crystalline solid to a mesophase [127]. Transitions to isotropic liquid occur above 200°C, a temperature at which thermal decomposition of the sample begins, and so they are difficult to detect.

This mesophase has been identified by means of X-ray diffraction as a columnar discotic mesophase, characterized by a two-dimensional hexagonal lattice (D_{ho}), as represented in Fig. 44(a). X-Ray diffraction patterns give a value of about 4.7 Å for the stacking period within the columns, and an intercolumnar distance of 20 Å (for laurate). EXAFS studies [129] reveal that, in the D_{ho} mesophase, each copper atom is surrounded by five oxygen atoms (average distance 2.05 Å), by one "proximal" copper atom (2.6 Å) and by one "distal" copper atom (3.2 Å) belonging to the adjacent dimer. These data indicate that the polymeric chain structure of the crystalline phase is retained in the columnar mesophase. The "crankshaft-like" arrangement of the dimers within the columns shown in Fig. 44(b) is proposed.

Magnetic susceptibility measurements [130] performed on these complexes gave values lower that those obtained for mononuclear copper(II) complexes due to anti-ferromagnetic intradimer electronic interactions. Interestingly, the value found for the singlet–triplet separation is significantly higher in the discotic phase than in the crystal, and this change is reversible as the temperature decreases. Hence, magnetic susceptibility provides a sensitive probe for the thermotropic phase transitions in these complexes.

Dinuclear Cu(II) complexes with branched carboxylates as ligands [131] also exhibit a D_{ho} mesophase which is stable for temperatures in the range of −20 to 200°C. Treatment of these complexes with a bidentate N-donor ligand such as pyrazine or 4,4′-dipyridyl yields compounds in which these ligands bridge dimeric copper units. These materials are formulated as oligomeric/polymeric species and

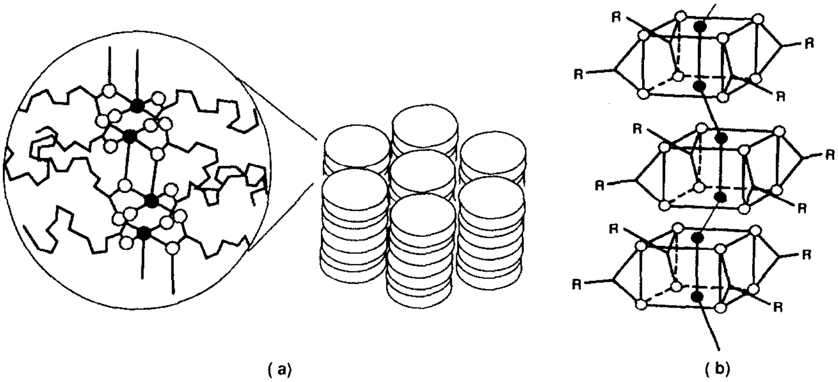


Fig. 44. (a) Schematic representation of the hexagonal columnar mesophase of copper(II) alkanoates. Adapted from ref. 127. (b) Proposed arrangement of copper(II) dimers within the columns. Adapted from ref. 129.

show a mesophase which could not be identified by X-ray diffraction. As in their parent complexes, the mesophase extends below room temperature. The pyrazine derivatives decompose at approximately 150°C by cleavage of the Cu—N bonds, whereas the 4,4'-bipyridyl complexes are stable up to their clearing temperature (about 154°C).

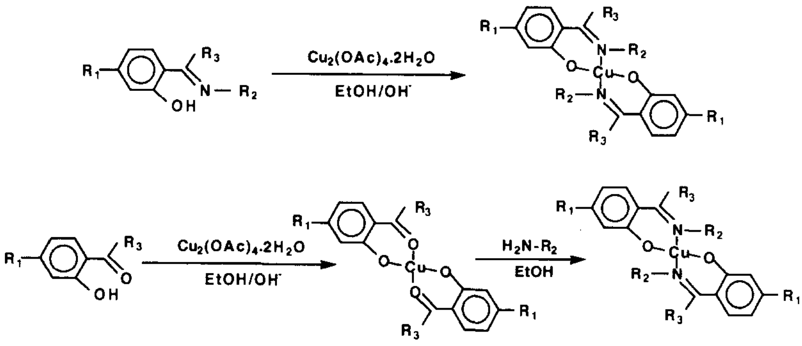
(c) Complexes with Schiff's base imines

Schiff's base chelating imines have been widely used as ligands in the preparation of mesogenic Cu(II) complexes. The synthesis of the Schiff's bases strongly depends on the nature of their substituents. Complexes can be conveniently prepared by either of the two routes shown in Scheme 6 [132,133].

Figure 45 shows the X-ray crystal structures of two mesogenic Cu(II) complexes with salicylaldimines as ligands. Complex A [134] has two crystallographically independent molecules **a** and **b**, which differ from each other mainly at the conformational level. The coordination geometry is strictly square-planar in molecule **a**, but distorted towards a tetrahedral pattern in molecule **b**. The N-bonded phenyl group is staggered with respect to the salicylaldiminate group between 46° (**a**) and 70° (**b**) and so, the overall molecular shape is lath-like rather than disc-like. The copper coordination geometry in complex B is not planar [135]. The two chelate planes form a torsional angle of 21.9°. The copper atom shows an intermolecular "contact" (3.04 Å) with the oxygen atom of an adjacent molecule ester group, as occurs in many other complexes with N,O-chelating ligands [136].

Due to the diversity of R substituents that can be introduced, a great variety of these mesogenic complexes has been reported. These compounds exhibit calamitic mesophases and show good thermal stabilities. Derivatives in which $R_3 \neq H$ (Scheme 6) are not mesogenic (henceforth we will assume $R_3 = H$).

The simplest derivatives that have been reported contain an alkyloxy chain in R_1 and an alkyloxyphenyl group in R_2 [99]. These complexes form S_A and S_C mesophases, identified by X-ray diffraction and textural observations. The layer



Scheme 6. Two synthetic routes for obtaining 4-substituted salicylamine copper(II) complexes.

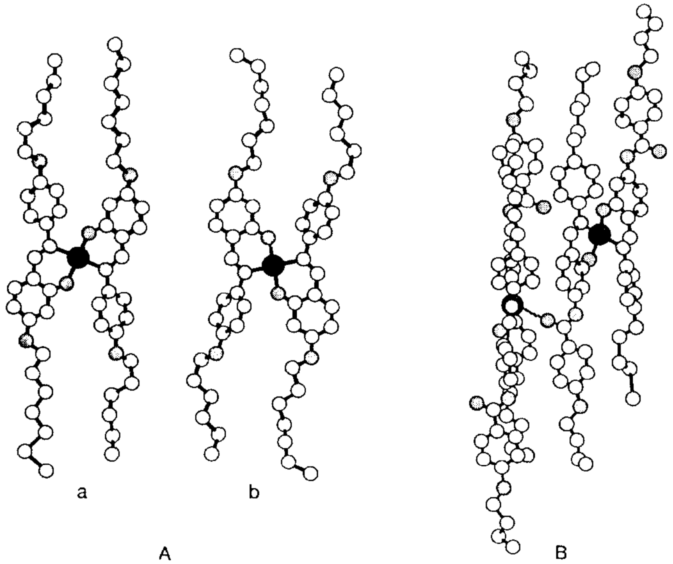


Fig. 45. (A) Structure of the two crystallographically independent molecules of [Cu(5-$C_8H_{17}O-C_6H_3(O)$-2-($CH=N-C_6H_4$-4'-OC_6H_{13}))$_2$]. Adapted from ref. 134. (B) Structure of [Cu[5-(4-$C_4H_9O-C_6H_4-CO_2$)-$C_6H_3(O)$-2-($CH=N-C_6H_4$-4'-OC_6H_{13})]$_2$]. Adapted from ref. 135.

thickness experimentally found in the S_A phase of the $R_1=OC_7H_{15}$ and $R_2=C_6H_4$-4-OC_6H_{13} complex (Fig. 45(A)) is 26.1 Å, slightly smaller than the molecular length in the crystal phase. This has been attributed to the presence of a conformational disorder in the terminal tails, a phenomenon that persists in the crystal phase, preventing a satisfactory resolution of the crystal structure. Polymers based on monomeric units similar to these complexes also show smectic mesophases [137].

Complexes with $R_2=C_6H_4$-4-C_nH_{2n+1} are also mesogenic [81,133], producing smectic mesophases but at lower temperatures. When a long chain is present in any of the R substituents, the complexes show a rich smectic polymorphism. Figure 46 shows the DSC thermogram obtained for the $R_1=OC_4H_8$ and $R_2=C_6H_4$-4-$C_{12}H_{25}$ complex. X-Ray diffraction experiments carried out on aligned samples of this compound [138] reveal an overlapping of the chains, giving interdigitated smectic layers for the S_E and S_B phases. The transition towards the S_A mesophase implies a melting of the paraffinic chains and an orientational disordering of the molecules around their long axis, but the interdigitated packing is retained. The diffraction patterns show a weak peak at 8.5 Å, attributed to Cu–Cu interferences. This molecular packing has been described in terms of pairs of molecules in a side-by-side array.

The mesogenic behaviour of several Schiff's base Cu(II) complexes with ester-type R substituents is summarized in Table 2. The unusual influence of apparently minor modifications on the mesogenic behaviour in the $R_1=O_2C_6H_4$-4-$OC_{14}H_{29}$, $R_2=C_nH_{2n+1}$ derivatives [141] deserves further comment. The series starts with an

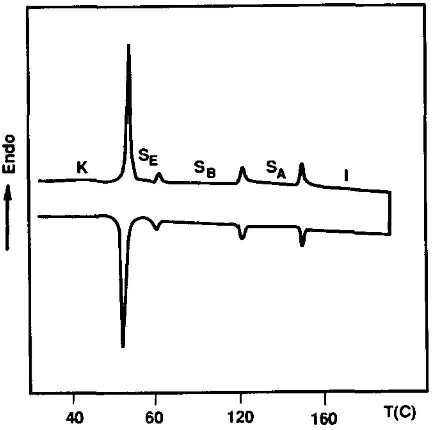


Fig. 46. DSC thermogram (heating and cooling cycle) of the complex $[\overline{\mathrm{Cu(5\text{-}C_4H_9O{-}C_6H_3(O)}}{-}2\text{-}(\mathrm{C{=}N{-}C_6H_4{-}4'\text{-}C_{12}H_{25}}))_2]$. Adapted from ref. 133.

S_C complex ($n=1$), whereas the $n=2$ derivative is not mesogenic. A nematic mesophase is obtained for $n \geqslant 3$, in contrast to the very general trend that favours smectic mesomorphism as the length of the chains increases. The S_C mesophase shows up again when $n=15$. X-Ray diffraction experiments reveal a layer thickness of 36.5 Å for the S_C phase of the $n=15$ complex, remarkably lower than the smectic periodicity measured for the $n=1$ complex (43.3 Å). This feature clearly indicates that, notwithstanding the phase homology, the molecular packing within the smectic layers must have undergone a significant change.

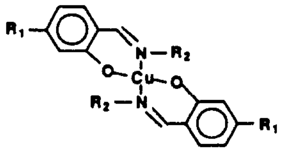
As far as the mesogenic behaviour is concerned, the main feature of the complexes collected in Table 2 is the formation of tilted smectic phases (S_C) rather than S_A, which only arises when both the R_1 and R_2 substituents contain ester groups. Hoschino et al. [135] have reported a tilt angle of 50° for the $R_1 = O_2C_6H_4$–4-OC_4H_9, $R_2 = C_6H_{13}$ complex S_C mesophase. The fact that the S_C phases change directly to either nematic or isotropic without going through S_A phases may be related to these large tilt angles.

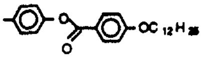
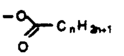
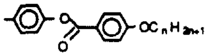
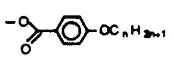
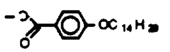
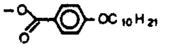
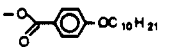
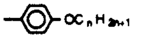
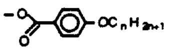
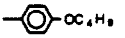
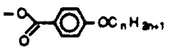
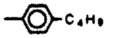
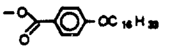
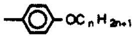
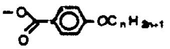
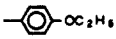
Complexes in which the R_1 substituents are in position 5 of the salicylenaldiminate ring have an overall shape markedly different from that of the compounds discussed above as a consequence of the different substitution [142]. These complexes display mesophases (N and S_C) only when $R_2 = CH_3$. Their parent 5-(4-alkyloxybenzoyloxy)-salicylaldehyde complexes also show mesogenic behaviour [145]. Some non-mesogenic tetradentate Schiff's bases also give mesogenic compounds when complexing copper [72,73]. The complexes shown in Fig. 47 show S_A mesophases below their decomposition temperatures (270°C).

Some mesogenic polymers based on copper(II) Schiff's base units have been reported [137,146–148]. As occurs in the monomeric complexes, polymers exhibiting nematic mesomorphism can be easily oriented in the mesophase with a magnetic field. The orientation of the molecules with respect to the field depends on the

TABLE 2

Mesogenic behaviour of Schiff's base copper(II) complexes



R_1	R_2	Mesophases	Ref.
$-OC_7H_5$		N	139
		n = 6; S_A+S_C (m)[a] n = 7; S_A+S_C n = 8 -12; S_C	99
	$-CH_3$	n = 6 - 9; N n = 10 -13; $N+S_C$ n=14; S_C	140
	$-C_nH_{2n+1}$	n = 1; S_C n = 2; no mesogenic n = 3 - 9; N n = 10,11; $N+S_C$ (m)[a] n = 13,14; $N+S_C$ n = 15; S_C	141
	$-C_nH_{2n+1}$	n = 1; $N+S_C$ n = 2 -10; N	70
		$N+S_C$	142
		N	143
		N	144[b]
		Smectic	143
		n = 6 -10; N n = 11-14; $N+S_C$ n = 16,18; S_C	135

[a] (m) = monotropic. [b] The effect of halogen substituents in the 3 or 5 salicylaldiminate ring positions is discussed. Halogenated complexes show shorter nematic ranges than non-halogenated.

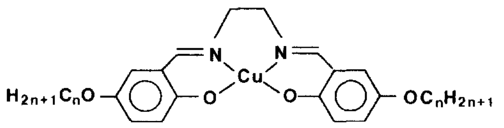


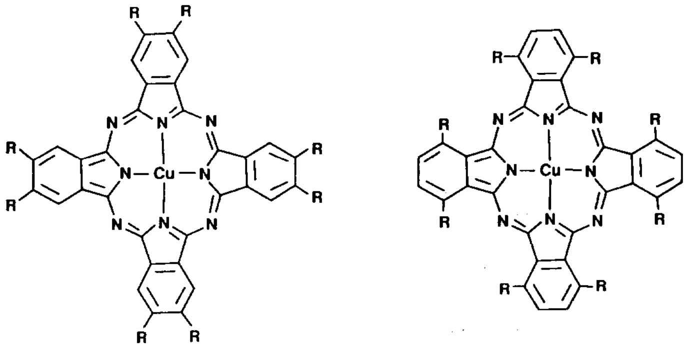
Fig. 47.

anisotropy of their magnetic susceptibility, and has been studied in connection with potential new applications. Two effects contribute mainly to the anisotropy of the magnetic susceptibility: the contribution of the paramagnetic entity due to the anisotropy of its g-tensor, and the strong diamagnetic susceptibility of the aromatic rings. A compromise between them is responsible for the actual orientation of the whole molecule in the presence of a magnetic field. In contrast to the vanadyl complexes already described (Sect. B), copper compounds have a high g-tensor anisotropy, which provides a strong anisotropic paramagnetic contribution to the molecular magnetic susceptibility [23,139,145,149]. Thus, the orientation of the nematic moiety (complex or polymer) in the magnetic field can be controlled by varying the number of aromatic rings or by changing the paramagnetic unit [150].

(d) Complexes with macrocyclic ligands

As it has been already mentioned for Co(II), phthalocyanine-type tetradentate ligands are capable of forming mesogenic complexes with several M(II) ions. Copper(II) complexes can be obtained by the general procedure shown in Scheme 1 (Sect. D.(i)) when copper cyanide is added in excess [151]. Alternative routes have been reported for some specific substituents [152]. These complexes exhibit a planar geometry, such as that found for copper(II)phthalocyanine [153]. When paraffinic substituents are present in the macrocyclic ligand, a molecular packing similar to the β-form of copperphthalocyanine is commonly assumed [154]. In this β-form, the molecules stack in columns with their molecular planes tilted against the perpendicular plane of the column.

Copper(II) complexes containing $R=CH_2{-}O{-}C_{12}H_{25}$ chains (Fig. 48(a)) exhibit on heating a transition from a room-temperature solid crystalline phase to a viscous, birrefringent mesophase [155] which is apparently stable up to about 300°C, where the product starts to decompose. The structural parameters of this mesophase have been determined from X-ray diffraction experiments being in agreement with a two-dimensional hexagonal lattice of columns (D_{ho}). The distance found between neighbouring columns (34 Å) is quite in accordance with the expected molecular parameters of the constituting molecules. The stacking period of the macrocyclic units within columns is 4.9 Å. The same structural arrangement is found in the mesophase of the $R=OC_nH_{2n+1}$ complexes, with a slightly smaller stacking distance (3.5 Å) [156].



(a) (b)

Fig. 48.

This compact stacking should increase the cooperative effects between the metallophthalocyanine subunits (ferro- and antiferromagnetism, ferroelectricity, exciton transfer, semiconducting properties). According to this, preliminary investigations carried out in such systems showed good perspectives for designing materials useful in the domains of electronics [157,158] and opto-electronics [159]. Interesting mesogenic and physical properties have also been reported for phthalocyanine copper complexes containing chiral [160] or crown-ether macrocyclic [161] substituents.

Phthalocyanine Cu(II) complexes in which the R substituents lie in mutually para positions (Fig. 48(b)) can be prepared by a procedure substantially different from that shown in Scheme 1 [162]. The uncomplexed macrocyclic ligands containing alkyl R chains exhibit mesomorphism, while derivatives with alkyloxy substituents do not. Complexation of the alkyl-chained ligands to copper remarkably widens the mesogenic ranges since the clearing temperatures increase about 100°C, whereas the melting points remain essentially unchanged. Figure 49 summarizes the mesogenic behaviour of these Cu(II) complexes. The D_1 and D_2 phases have been assigned a hexagonal columnar and a rectangular columnar lattice, respectively, based on their microscopical textures, whereas D_3 has not been identified.

Other macrocyclic ligands also give mesogenic Cu(II) complexes. Thus, copper compounds containing octa-substituted porphyrins form hexagonal columnar meso-

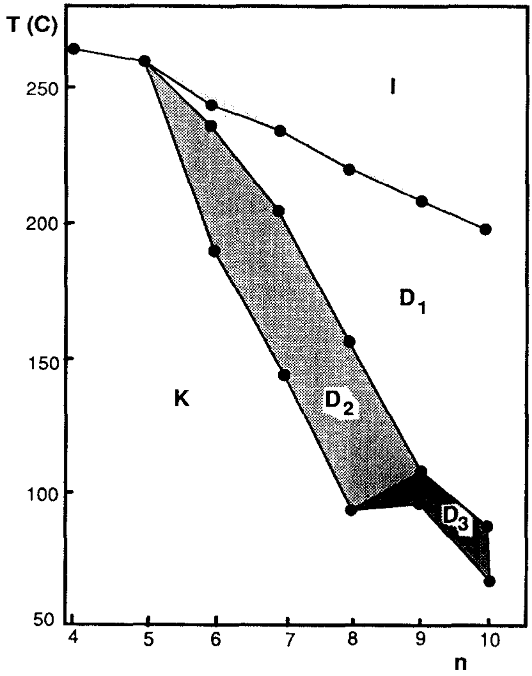


Fig. 49. Transition temperatures as a function of the alkyl chains length of the copper(II) 1,4,8,11,15,18,22,25-octaalkyl phthalocyanines. Adapted from ref. 162.

phases, whereas (octa(dodecyl)tetrapyrazinoporphyrazino)copper(II) exhibits a phase identified by X-ray diffraction as a disordered rectangular columnar mesophase [33,163]. Copper (II) complexes with annelide-type ligands give rise to organized phases, so-called tegma crystals [164].

G. d^{10} ELECTRONIC CONFIGURATION

The metallic ions of this configuration which form stable complexes are Cu(I), Ag(I), Au(I), Zn(II), Cd(II) and Hg(II), and mesogenic complexes have been reported for all of them. Since the d^{10} configuration affords no crystal field stabilization, the stereochemistry of these complexes depends on factors such as the size and polarizing power of the cation or the steric requirements of the ligands. The heavier cations most commonly form two coordinate linear complexes as occurs in silver(I) salts and in organometallic Hg(II) derivatives. This linear geometry is, in principle, very suitable to give mesogenic compounds. On the other hand, both Zn(II) and Cd(II) favour four-coordinate tetrahedral complexes, although many examples of other stereochemistries are known.

(i) Silver(I) complexes

The bis-stilbazole silver(I) complexes represented in Fig. 50 can easily be obtained by reaction of the stilbazole ligand with a soluble silver salt [165].

Many of these salts show mesophases with transition temperatures depending on the counterion Y^-. Thus for BF_4^-, the mesophase transitions are high and close to the decomposition temperatures. However, salts with $C_{12}H_{25}SO_3^-$ melt at much lower temperatures showing nematic phases for $n = 1$–4, while S_A and S_C phases are found for $n \geqslant 4$ [102].

The non-mesogenic 4-pyridylmethylene-4′-alkyloxyanilines and 4′-alkyloxyphenyl-4-pyridylcarboxylates also form mesogenic silver(I) salts with several anions (BF_4^-, NO_3^-, PF_6^-, $CF_3SO_3^-$) [166]. These compounds display nematic S_A and S_C mesophases, along with other more ordered non-identified viscous phases. For these ionic complexes, the nature of the central group of the ligand largely influences the type of mesophase and the mesogenic ranges, although the existence or absence of mesomorphism depends essentially on the chain length. However, the main influence in the mesogenic properties comes from the nature of the anion. Thus, the less

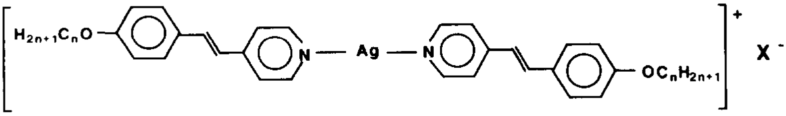


Fig. 50.

voluminous the anion, the broader the mesophase range and the lower the melting point.

Some of these silver salts were the first examples of ionic materials showing thermotropic nematic phases [167].

Alkylamines also form liquid crystalline cationic compounds when complexing silver. Stoichiometric reaction of alkylamines with soluble silver salts in acetonitrile yields salts $[Ag(H_2NC_nH_{2n+1})_2]X$ ($X = NO_3^-$, BF_4^-, $CH_3CO_2^-$) [168]. The complexes exhibit thermotropic S_A mesophases at low temperatures which, for $X = CH_3CO_2^-$, reach −26°C. In addition, these complexes show lyotropic liquid crystal behaviour, giving rise to lamellar mesophases. The structures of these liquid crystalline phases have been determined by X-ray diffraction in magnetically aligned samples and consist of a double layer of U-shaped cations sandwiching a central layer of anions. These complexes represent the first example of transition metal mesogens showing lyotropic, in addition to thermotropic, behaviour whose mesophases have been fully characterized.

Silver primary thiolates $AgSC_nH_{2n+1}$ have, in the solid state, a bilayer structure consisting of a central plane of silver atoms in a hexagonal arrangement, connected by bridging μ^3-SR groups perpendicular to the silver plane on both sides (Fig. 51), for $n = 4$–18. On heating, they display successively lamellar (smectic A), cubic and micellar mesophases, the ranges of the first two decreasing with increasing length of R, so that, for $n \geqslant 12$, only the micellar phase is observed. X-Ray diffraction on the mesophase of the compound with $n = 18$ shows that it is a hexagonal columnar mesophase, understood to be the result of packing cyclic molecules

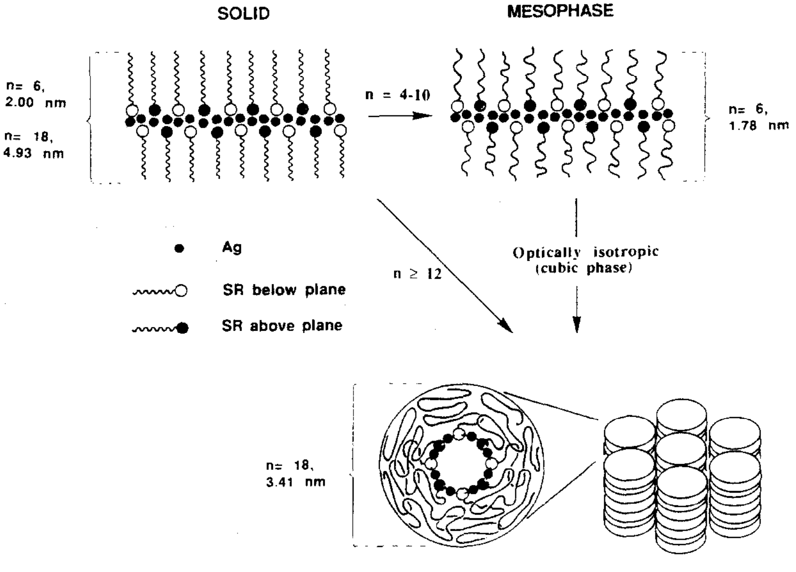


Fig. 51. Schematic representation of the solid state and mesophase molecular arrangement of the complexes $[AgSC_nH_{2n+1}]$.

$[AgSC_{18}H_{37}]_8$, where the silver atom has a linear coordination and the thiolates act as μ^2-bridging groups. This kind of cyclic structure is known in the solid state for thiolates with bulky (secondary or tertiary) chains, so that the structural change is attributed to the steric effect produced by the melting of chains in the mesophase. Copper(I) thiolates behave quite similarly and are the only Cu(I) mesogens reported so far [169].

(ii) Gold(I) complexes

Figure 52 shows the proposed structure of the only mesogenic gold(I) complex reported [101,102]. The compound exhibits a non-identified mesophase between 120 and 200°C, the temperature at which it starts to decompose.

(iii) Zinc(II) complexes

Macrocyclic complexes (Fig. 53) can be obtained by reaction of zinc acetate and the corresponding porphyrin in refluxing ethanol [170].

When $R = CO_2{-}C_nH_{2n+1}$, the complexes obtained display discotic mesophases, only one for the $n = 4$ derivative or two different ones for $n = 6$, 8. Although these mesophases have not been characterized, their textures resemble those of columnar phases exhibited by other macrocyclic metallic complexes [163]. Derivatives with $R = CH_2{-}O{-}C_nH_{2n+1}$ [170] show a single fluid columnar mesophase in the temperature range of about 60°C, even when the free ligands do not form liquid crystalline phases or do so over small temperature ranges. Similar derivatives have also been obtained with other metals. Comparison reveals that the nature of the metal plays an important role in the appearance and temperature range of the liquid crystalline

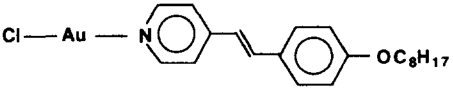


Fig. 52.

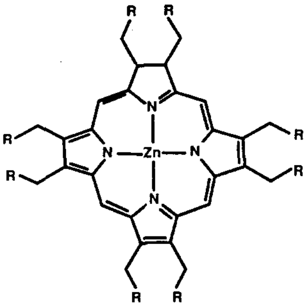


Fig. 53.

phase. This behaviour contrasts with that of the octa-ester derivatives, where the presence or absence of a metal has only subtle effects on the thermal transitions.

Some other macrocyclic ligands are also capable of forming mesogenic complexes with zinc, giving rise to hexagonal columnar mesophases [32,33].

Similar to Ni and Pd, Zn(II) complexes with two dithiobenzoate ligands ($[Zn(S_2C{-}C_6H_4{-}4{-}OC_nH_{2n+1})_2]$) also display mesomorphism [102]. The X-ray structure determination of the $n=4$ complex shows it to be dinuclear (Fig. 54) containing an 8-membered $Zn_2C_2S_4$ ring with a distorted trigonal bipyramidal geometry about the zinc, in contrast to the monomeric structure found in the related $[Zn(S_2C{-}C_6H_5)_2]$ complex [171]. These Zn(II) complexes display only nematic mesophases, showing a difference from their parent Pd and Ni derivatives which give rise both to nematic and to smectic phases.

A family of mesogenic salts of general formula $[(C_nH_{2n+1}NH_3)_2(ZnX_4)]$ (X = Cl, Br) has been reported [172]. Such compounds contain the transition metal atom in the form of a ZnX_4^{2-} counterion and display smectic mesomorphism.

(iv) Cadmium(II) complexes

As a part of a broad study of the mesogenic activity of alkaline and alkaline earth soaps containing long-chain alkanoates as ligands, Spegt and Skoulios [173] have reported the mesogenic behaviour of $[Cd(O_2C{-}C_nH_{2n+1})_2]$ complexes. The investigated compounds ($n=12$–20) exhibit a discotic mesophase between 100 and 200°C. The X-ray characterization of these phases reveals that molecules are grouped in cylindrical structural elements which form a two-dimensional hexagonal array.

Cd(II) porphyrin complexes with eight ether R substituents, similar to those mentioned above for Zn(II) (Fig. 53), display discotic mesomorphism but in narrower temperature ranges than their Zn(II) homologues [163].

(v) Mercury(II) complexes

The organometallic mercury(II) derivatives represented in Fig. 55 (p. 263) were the first reported liquid crystalline transition metal complexes [174].

The complexes were obtained by condensation of bis-(4-aminophenyl)mercury with aromatic aldehydes. Derivatives with R = H, CH_3, $CH{=}CH_2$ and OC_nH_{2n+1}

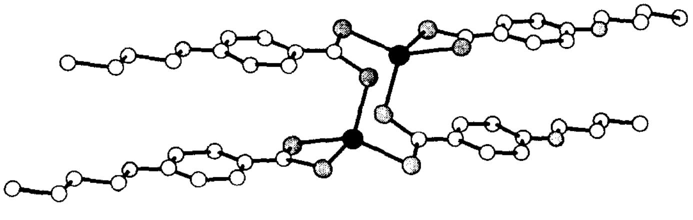
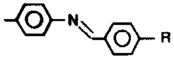
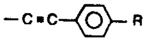
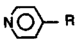
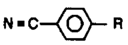
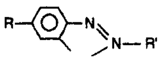
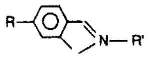
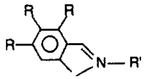
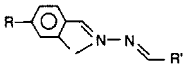
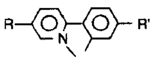
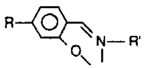
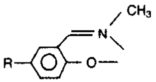
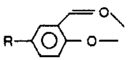
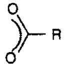
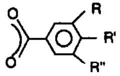
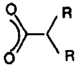
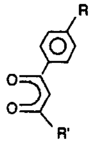
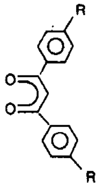
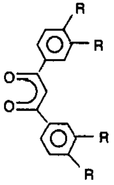


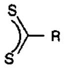
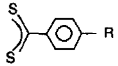
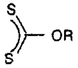
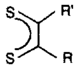
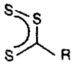
Fig. 54. Structure of $[Zn_2(S_2C{-}C_6H_4{-}4{-}OC_4H_9)_4]$. Adapted from ref. 102.

H. TRANSITION METAL LIQUID CRYSTALS. TABLE OF COMPLEXES ARRANGED BY LIGAND TYPE

Promesogenic ligand	Donor atom	Metal	Coordination	Mesophase	Observations	Ref.
	C	Hg(I)	Linear	S	First TMLC (1923)	174
	C	Pt(II)	Square-planar	N, S_A	Thermotropic monomers, lyotropic polymers	105,106
H_2N-R η^2-CH=CHR	π-C_2	Pt(II)	Square-planar	S_A		103
	N	Ag(I)	Linear	S_A, Neat	Amphotropic. Lowest mesophase temperature reported. Cationic complexes, anions: BF_4^-, NO_3^-, OAc^-	168
	N	Rh(I)	Square-planar	N, S_A		45,46
	N	Rh(I)	Octahedral	?	Tetranuclear cluster. Mesomorphism not confirmed	47,48
	N	Ir(I)	Square-planar	N, S_A		46,49,50
	N	Pd(II)	Square-planar	N, S		103
	N	Pt(II)	Square-planar	S_A		103
	N	Ag(I)	Linear	N, S_A, S_C, ...	Cationic complexes; anions: $C_{12}H_{25}SO_3^-$, $CF_3SO_3^-$, BF_4^-, NO_3^-, PF_6^-	101,102, 165–167
	N	Au(I)	Linear	?		101,102
	N	Rh(I)	Square-planar	N, S_A		44
	N	Pd(II)	Square-planar	N, S_A, S_C		44,101,102
	N	Pt(II)	Square-planar	N		44,101,102
S-R	S	Ag(I)	Linear/trigonal	Lamellar/ D_h micellar	Covalent soaps	169
	π-C_4	Fe	"pentacoordinated"	N, S_A	Chiral metal centre	41
	π-C_5	Fe(II)	"sandwich"	S_A, S_C		27,28

Promesogenic ligand	Donor atom	Metal	Coordination	Mesophase	Observations	Ref.
	C, N	Pd(II)	Square-planar	N, S_A, S_B	Halogen-bridged dinuclear and mononuclear complexes	77–79, 81–83
	C, N	Pd(II)	Square-planar	N, S_A, S_C	X-bridged dinuclear complexes (X = Cl, Br, SCN, OAc) and mononuclear complexes	84–86, 88–90
	C, N	Pd(II)	Square-planar	N_D	X-bridged dinuclear and tetranuclear complexes. (X = Cl, Br, SCN, OAc)	91
	C, N	Pd(II)	Square-planar	N, S_A, S_C, S_C^*	X-bridged dinuclear complexes (X = Cl, Br, SCN, O_2C-R) First ferroelectric TMLC	93–95
	C, N	Pd(II)	Square-planar	N, S	Halogen-bridged dinuclear complexes and neutral and cationic mononuclear complexes	97,98
	N, O	V(IV) [VO^{2+}]	Square-pyramidal	N, S_A	Paramagnetic mesophases	21,23
	N, O	Fe(III)	Octahedral?	S_A	Paramagnetic mesophases	24
	N, O	Ni(II)	Square-planar	N	R′ = alkyl	70
	N, O	Ni(II)	Square-planar	S	R′ = -CH_2-CH_2-	72,73
	N, O	Pd(II)	Square-planar	S_A, S_C		99,100
	N, O	Cu(II)	Square-planar octahedral?	N, S_A, S_C	Complexes of low and high molecular weight (Table 2, section 6)	23,70,72,73,81 99,132–135, 137–144,146–149
	N, O	Cu(II)	Square-planar	N, S_C		142
	O_2	Cu(II)	Square-planar	S_C		145
	O_2	Cr(II)	"Lantern structure"	D_h	Quadruple M-M bond	26

	O_2	Mo(II)	"Lantern structure"	D_h	Quadruple M-M bond	26
	O_2	Ru(II)	"Lantern structure"	D_h	Double M-M bond. Paramagnetic phases	29
	O_2	Ru(II), Ru(III)	Octahedral?	D_h	Paramagnetic phases	30
	O_2	Rh(II)	"Lantern structure"	D_h	M-M bond	36–38
	O_2	Cu(II)	"Lantern structure"	D_h		126,127, 129,130
	O_2	Cd(II)	?	D_h micellar	Soap	173
	O_2	Rh(II)	"Lantern structure"	D_r, D_h	The number of terminal chains determines mesophase type	39
	O_2	Cu(II)	"Lantern structure"	D_h		131
	O_2	Cu(II)	Square-pyramidal	?	Oligomeric pyrazine and 4,4′-bipyridyl adducts	131
	O_2	Pd(II)	Square-planar	?	Mesomorphism not confirmed	104
	O_2	Cu(II)	Square-planar	N	Biaxial phases	111,112 123,124
	O_2	Fe(III)	Octahedral	?	Mesomorphism not confirmed	25
	O_2	Cu(II)	Square-planar	D_L	Tilted mesophase	109,115,116, 118–122
	O_2	Cu(II)	Square-planar	D_h		110,113,114

Promesogenic ligand	Donor atom	Metal	Coordination	Mesophase	Observations	Ref.
	S_2	Ni(II)	Square-planar (Square-pyramidal?)	lamellar	Dinuclear complexes R = alkyl	55
	S_2	Ni(II)	Square-planar	S_C, S_H		58
	S_2	Pd(II)	Square-planar	N, S	Associate in dimers in solid state	102
	S_2	Au(III)	Square-planar	S_A		102
	S_2	Zn(II)	Trigonal bipyramidal	N	Dinuclear complexes	102
	S_2	Ni(II)	Square-planar	ordered S		55
	S_2	Ni(II)	Square-planar	N, S_C	$R'=H$; $R=\text{-}C_6H_4\text{-}4\text{-}R''$	65,66
	S_2	Ni(II)	Square-planar	D_h	$R=R'=\text{-}C_6H_4\text{-}3,4\text{-}R''_2$	67
	S_2	Pt(II)	Square-planar	N, S_C	$R'=H$; $R=\text{-}C_6H_4\text{-}4\text{-}R''$	66
	S_2	Ni(II)	Square-planar	N	$R=\text{-}C_6H_4\text{-}4\text{-}R'$	58
Substituted porphyrine	N_4	Co(II)	Square-planar	D_h,?		32,33
	N_4	Cu(II)	Square-planar	D_h		33,163
	N_4	Zn(II)	Square-planar	D_h		32,33 163,170
	N_4	Cd(II)	Square-planar	D_h		163
Substituted phthalocyanine	N_4	Co(II)	Square-planar	D_h		31
	N_4	Co(III)	Octahedral	D_h	Anionic and polymeric complexes	31
	N_4	Cu(II)	Square-planar	D_h, D?		155,156 160–162
Substituted tetrapyrazinoporphyrazine	N_4	Cu(II)	Square-planar	D_r		163
	Br	Zn(II)	Tetrahedral	S	Ionic compounds containing	172

have been prepared, all of them showing smectic mesophases. The related complexes [X–Hg–C_6H_4–4-N=CH–C_6H_4–4′-OCH_3] (X = O_2CCH_3, Cl) are also mesogenic.

I. COORDINATION GEOMETRY, MOLECULAR SHAPES AND PROPERTIES OF TRANSITION METAL LIQUID CRYSTALS

In the preceding pages, we have offered a comprehensive up-to-date review of liquid crystals based on compounds containing d^1–d^{10} metals (TMLC, transition metal liquid crystals). A quick glance to the references will reveal that, with very few exceptions, the compounds are less than 15 years old, and most of them have been reported during the last 5 years. Since the synthetic methodologies used are obviously older, this late development may have been due to neglect or ignorance on the topic by coordination chemists. The recent explosion of interest in this field is due to the effort of a very small number of teams, either of scientists who originally worked on organic liquid crystals and then have stepped forward to introduce metals into their molecules or of inorganic chemists who have moved to work with promesogenic ligands in the metal systems most familiar to them. As a consequence, these efforts have very much concentrated on the most promising molecular geometries, usually mimicking successful organic systems, and on chemical systems known to be particularly stable and accessible, but it is unlikely that the present panorama is representative of what transition metal mesogens can really offer.

Almost without exception, the TMLC reported so far are thermotropic systems based on monomeric or oligomeric neutral molecules. In this context, the art of making a TMLC is the art of building molecules with intermolecular interactions strong enough to induce an orientational order but weak enough to allow this situation to be reached below temperatures which can either affect the integrity of the molecule (decomposition) or overcome any intermolecular orientational forces (isotropic liquid). This presents the TMLC chemist with the rather difficult task of guessing melting points, which justifies the use of the word “art”.

Compared with the usual organic compounds, coordination compounds produce stronger intermolecular interactions by means of intermolecular contacts (whenever a coordination site is accessible) and strong dipolar interactions (associated with the high polarizability of transition metals), which are responsible for their usually high melting points. This increase in interactions is well illustrated by the fact that introduction of a transition metal fragment (such as *cis*-[RhCl$(CO)_2$]) in a non-mesogenic ligand induces the appearance of liquid crystallinity (Sect. E.(ii), ref. 45).

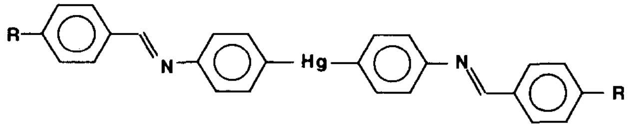


Fig. 55.

Whereas in organic liquid crystals the question is frequently to increase intermolecular interactions to produce liquid crystallinity, the problem in TMLC is often to prevent these intermolecular interactions from being so strong as to lead to undesirably high melting points; this can be accomplished by using long alkyl or alkyloxy tails that hinder intermolecular forces extending in the three dimensions, and by introducing some irregularity in the molecular shapes to avoid a perfect packing leading to too strong intermolecular interactions.

On the other hand, a liquid crystal is a mobile anisotropic packing of molecules (with orientational but not positional order) which can be induced by using molecules with anisotropic shapes, usually rod- (lath-) or disc-shaped molecules. In the eyes of a coordination chemist, geometry immediately recalls coordination geometry, so that rod-shape suggests linear coordination and disc-shape evokes square-planar coordination. While many examples in the preceding sections appear to support this view (and have probably been conceived having this idea in mind) there are sufficient examples to illustrate that, in reality, molecular shape refers to the whole molecule in mesophase conditions (which usually means a vibrationally excited state), and the coordination sphere is generally no more than the inner core of a molecule bearing rather bulky substituents. Compatible with any core geometry, there are often different possibilities for chain distribution, which will eventually define the overall shape of the molecule; the distribution chosen is, apparently, that able to fill the space more efficiently. Perhaps the importance of the coordination geometry has been overvalued and one can expect to obtain liquid crystals based on apparently less favourable coordinations, such as tetrahedral or octahedral, provided that the ligands are adequately designed.

The determinant influence of the chains and the requirement of efficient space filling can be illustrated by the behaviour observed in different ortho-palladated systems (Sect. E.(v)). Thus, the planar halobridged dimers arising from ortho-palladation of azobenzenes, imines, or azines with chains in their para positions (eqn. (3), Scheme 4, Figs. 27(a) and 30) give rise to calamitic liquid crystals because the chains, rather than filling a disc-shaped plane inefficiently, extend parallel to each other in the two halves of the dimer defining an H, that is two "fused" rods. Even when the molecule is bent, as in the carboxylato-bridged dimers (Figs. 27(b) and 32), the dominant overall shape is that of two (or three, for long carboxylates) fused rods, producing a typical calamitic behaviour. However, if more chains are introduced in the "in plane" ortho-palladated ring (Fig. 29) these efficiently fill the space around the coordination plane in a disc-like distribution and nematic–discotic behaviour is obtained. A similar case is found when comparing the discotic behaviour of the Ni(II) complex in Fig. 23 with the calamitic properties of those in Fig. 22.

A more dramatic example is provided by the behaviour of silver primary thiolates (Fig. 51) which in the solid state adopts a bilayer structure for $n = 4$–18. On melting, a lamellar bilayer structure (S_A) is produced for $n = 4$–10, whereas a columnar micellar mesophase is formed for $n \geqslant 12$. This different behaviour is due to the different steric requirements of short or long chains in the mesophase (not in the solid) which are able to induce a change in the coordination geometry of silver (from 3-coordinated to linear) and in the coordinating mode of the thiolate (from μ^3- to μ^2-bridging). This example also illustrates that the solid state structure is not necessarily a good indication of the molecular shape or even of the molecular structure in mesophase conditions.

The different ionic mesogens $[AgL_2]X$ in Sect. G.(i) are also interesting as an example of some peculiar aspects that have to be considered when working with long anisotropic substituents. In all cases, the silver coordination is linear, and when L is a 4-substituted pyridine ring, this determines the formation of a rather long linear rigid core so that the cation adopts an overall rod-like shape. However, when L is a primary amine, the chains are free to adopt a different orientation immediately after the linear N–Ag–N system, and at this short distance a U shape of the cation allows intra-cation interactions between the chains and a compact bilayer organisation with efficient chain-to-chain and cation-to-anion interactions; thus, in this case the linear coordination of silver does not determine a linear shape for the cation.

These ionic metallomesogens recall another interesting point. In general the chemist is used to thinking of ionic interactions as isotropic in nature. While this is generally useful when working with roughly spherical ions, this idea cannot be applied to the mesogenic species, as cations and anions can only approach each other in the directions sterically allowed by the ligands and the chains, which makes the ionic bond, in a sense, directional. Ionic metallomesogens have received little attention so far but they (and their possible lyotropism) are a characteristic sub-class which deserves more study. The silver amine complexes described above show thermotropic mesophases at very low melting points (−26°C for X = O Ac) in addition to lyotropic mesomorphism in water.

There are already many examples that suggest that metal-containing mesogens can tolerate stronger deviations from linear or planar shapes than organic mesogens. The vanadyl complexes (Fig. 8), the ferrocene derivatives (Fig. 10), the iron complexes in Fig. 13, the "lantern" complexes (Fig. 12), the open-book palladium complexes with short carboxylate bridges (Fig. 32), and the rather extraordinary rhodium cluster in Fig. 16 provided its mesogenic behaviour is confirmed, all have some parts of the molecule that span out of the plane in which the chains presumably lie; yet they are liquid crystals. Thus it is conceivable that the dominant, but so far rather neglected, octahedral coordination can be of more use to make liquid crystals, allowing the extension of the field to almost any transition metal.

In fact, although the first report of a purely octahedral liquid crystal complex [25] has not been confirmed, the Co(III) cationic complex in Scheme 2 is an indubitable example, and we note that quite a few complexes in this review have a hidden octahedral geometry. Thus, it is likely that the iron complex in Fig. 9, reported as pentacoordinated, has in reality a dimeric octahedral geometry using oxygen bridges (two octahedra sharing an edge); ferrocene has a formally octahedral coordination;

the same applies to the "lantern" complexes having a metal–metal bond and apical ligands. Intermolecular contacts expanding square-planar coordinations to octahedral are likely in Ni(II) and Cu(II) metallomesogens, and they are realised to the extreme in the polymeric Co(III) complex in Scheme 2, where the cyanide bridges are connecting octahedral corners and help to support a columnar structure, revealing just one of many possible ways to make a clever use of octahedral coordination for liquid crystals.

A correct balance in intermolecular interactions is the key problem to obtain liquid crystals and, as suggested before, the presence of a metal usually undesirably increases these interactions. For instance, the $[PdCl_2(NCR)_2]$ complexes show melting points many degrees higher than their free ligands, so that, at the mesophase temperature, the inherent lability of these nitrile complexes produces some decomposition [102]. Very often, metallomesogens suffer severe decomposition at their too high clearing point. This is a serious problem because many physical studies and applications require one to take the compound to their isotropic state. Very perfect shapes can lead to melting points so high that the compound goes directly to its isotropic state or decomposes before melting, as occurs in the apparently promising *trans*-$[RhCl(CO)(NC_5H_4{-}4{-}CH{=}N{-}C_6H_4{-}4'{-}OC_nH_{2n+1})_2]$ (Fig. 15). The fact that perturbing these shapes can produce good results is illustrated in the following examples.

Replacement of Cl by hexanoate noticeably reduces the melting points of the palladium nitrile complexes above [103]; similarly, cleavage of the H-shaped palladium dimers to P-shaped monomers [90] produces a large decrease in melting and clearing temperatures, allowing one repeatedly to go to the isotropic state without symptoms of decomposition; the use of branched carboxylates in the typical dinuclear Cu discotics has reduced the melting temperatures to $-20^\circ C$ [131]. This game, however, has a limit as shown by the disappearance of mesomorphism when in the complexes $[RhCl(CO)_2(NC_5H_4{-}4{-}CH{=}N{-}C_6H_4{-}4'{-}OC_nH_{2n+1})]$ one CO is replaced by $P(OMe)_3$ or two CO groups are replaced by COD. Surprisingly, the alkynyl platinum complexes in Fig. 36 [105] are liquid crystals in spite of having two PMe_3 ligands. Thus, where the limit is can only be determined by trial, which often takes less time than speculation.

Working in TMLC does not necessarily imply an interest in advanced materials. Since mesophases provide the molecules with such a different environment from that in the solid state or in solution, it necessarily should attract the structural scientist (and there is a real need for them in the field), the spectroscopist, and those working in many other physical properties of matter. It is a bit unfortunate that the topic has seen light when everybody knows that organic liquid crystals are materials. TMLC are asked to offer something useful even at this early stage, which is perhaps not fair since, after all, organic liquid crystals have had one century to evolve to their present state. It should be clear by now that remarkable advances have been achieved in the last few years in terms of the stability and the temperature range of

TMLC so that they will surely be able to match the performance of organic materials in the near future.

Some potential properties that TMLC offer (high polarizabilities, high birefringences) have already been found superior to the values met in related organic materials, in spite of the scarcity of studies on physical properties (again the number of liquid crystal physicists in the field is very low, compared with the attention paid to organic mesogens), holding promise for application in specific devices requiring ferroelectricity or non-linear optical behaviour. Other properties, such as colour, might not be very interesting, as organic dyes have provided an adequate solution. Chirality is easily introduced in TMLC by using chiral organic moieties, but it is interesting to prepare and test materials with chirality based on the metal centre, an idea already tried with the iron complexes in Fig. 13. A property that organic materials cannot offer as easily as TMLC is paramagnetism; the dominance of organic liquid crystals has produced commercial electro-optic displays presently based on electric fields (many TMLC seem to have some instability in electric fields), but it is equally possible to design devices based on magnetic fields, which exert good control on the orientation of paramagnetic TMLC.

Last, but not least, TMLC offer a way to induce, modify and control molecular arrangements of metal-containing molecules, and usually the order in the mesophase can be quenched by fast cooling. Moreover, their fluidity allows a processability unmatched by solid materials. There is a door open here to those looking for specifically ordered arrangements in the solid state, either as materials or as precursors. A new world to discover might be waiting for them beyond this door.

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