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Metal-containing liquid-crystal phases

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Abstract. Data on the synthesis, structures, and properties of ionic, coordination, organometallic, and organoelement compounds with liquid-crystal properties are surveyed. The substances examined are new in the chemistry of liquid-crystal compounds. Their potential applications are described. The bibliography includes 211 references.

I. Introduction

Liquid crystals have been known for more than 100 years but the number of structural types and of classes of chemical compounds capable of exhibiting mesomorphic properties has increased significantly only during the last 15 – 20 years. For example, discotic, columnar, and nematic phases,[1-3] cup-shaped liquid crystals,[4] and columnar associated species in which the molecules are linked by a system of hydrogen bonds have been added recently to the structural types of low-molecular-mass liquid crystals alone.[5,6] New classes of mesogenic chemical compounds include also coordination compounds, usually complexes of mesogenic ligands with various metals,[7,8] as well as certain organometallic and organoelement compounds. Furthermore, new data have appeared recently on salts of organic acids possessing mesomorphic properties, which have been known for a long time.[9]

Evidently the physical properties of the compounds listed above should differ from those of classical organic mesogenic substances. Thus metal containing mesogenic substances are usually paramagnetic and this leads to new possibilities for their practical use.

In the present review, we have attempted to survey data on the methods of synthesis (in those cases where they are not trivial), structures, and properties of new metal-containing mesogenic substances. Furthermore, we endeavoured to trace, wherever possible, the relation between molecular structure, type of packing in the crystal, and the nature of the existing intermolecular interactions, on the one hand, and the tendency manifested (or not manifested) by the given compound to form definite types of mesophases, on the other. Such analysis permits a deeper understanding of the characteristics of the structures of liquid crystal phases, the discovery in many cases of new types of mesophases, and also the prediction of the presence of mesogenic activity in specific compounds.

It is noteworthy that analysis of the authors' own studies occupies an appreciable place in the present review, since the studies by foreign investigators have been described in fair detail in the review of Giroud-Godquin and Maitlis.[7] Unfortunately, the latter review includes hardly any work published in Soviet journals and we believe that the present article should fill this gap.

In analysing the relevant data, one can employ different approaches to the classification of the test objects. We believe that it is most useful to arrange mesogenic metal-containing compounds in groups in the following way: ionic compounds, coordination compounds (the most numerous group which can be subdivided in terms of the types of ligands), organoelement compounds, and organometallic compounds. However, one should bear in mind the arbitrary nature of this classification and the possibility of assigning the same compound to different groups simultaneously.

We shall not dwell on the structural classification of the types of liquid crystals, since it has been described in fair detail in a monograph[10] and also in other reviews.[3,11] We shall restrict consideration to principal low-molecular-mass thermotropic liquid crystals, since high-molecular-mass as well as lyotropic liquid crystals constitute separate independent groups.

II. Metal-containing ionic liquid crystals

Ionic liquid crystals have long been known. A characteristic feature of these compounds — the possibility of the separate existence of the cationic and anionic components of the molecules in the mesophase (in contrast to molecular liquid crystals in which the metal is firmly coordinated to the ligand atoms) — gives rise to a series of new properties of such phases. Typical representatives of ionic liquid crystals are carboxylic acid salts.

1. Carboxylic acid salts

As early as 1910, Vorländer[12] first observed the liquid-crystal state on fusion of salts of long-chain carboxylic acids referred to as soaps.

Structural studies at high temperatures on the anhydrous thermotropic mesophases of a series of homologues of salts of long-chain aliphatic acids $C_nH_{2n+1}COOH$ (n = 9 – 19, odd values of n) have been described in a number of communications.[13-16] The following structures were established in these investigations on the basis of X-ray diffraction data: layered (smectic) structures with an ordered or disordered

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disposition of aliphatic chains, discotic structures with an orthogonal lattice (for example, in the sodium salts of aliphatic acids), and columnar (ribbon) structures with a hexagonal packing of the columns. In layers of homologues of the same metal, it is possible to observe the entire set of structural types described. For example, calcium carboxylates are characterised below 100 °C by a layered structure with the disposition of the alkyl chains at right angles to the plane of the layer, while in the range from 120 to 180 °C they are characterised by hexagonal packing of cylindrical associated species.[16] Unfortunately, X-ray diffraction studies on the mesophase do not permit the determination of the detailed pattern in the packing of the molecules in discs and cylinders[13-16] and the most likely hypotheses concerning their structures can be formulated only on the basis of X-ray diffraction studies of the corresponding single crystals.

At the beginning of the 1970s, it was observed that the homologues of the salts of lower carboxylic acids also exhibit thermotropic mesomorphism.[17] Their structures and thermodynamic, transport, and optical properties have been reviewed.[9]

The observation of mesophases in such compounds, which have been called ionic liquid crystals (ILC), was fairly unexpected since the presence of extended molecules, usually one of the main conditions for the manifestation of mesomorphism, is not characteristic of these substances. It is believed[9] that the species constituting these mesophases are quasi-globular associated formations containing metal cations (Na^+, K^+, Ba^{2+}, Tl^+, Cd^{2+}, Cs^+) and carboxylate anions (n-$C_nH_{2n+1}COO^-$, $2 \leqslant n < 7$). The latter do not exhibit an explicit anisometry (the length to width ratio does not exceed 2). Furthermore, in contrast to the classical molecular liquid crystals, ionic liquid crystals are characterised by a high ratio of the electrostatic charges on the constituent components to the total number of atoms, which leads to the predominance of Coulombic forces over van der Waals forces in the formation of their structure. Ionic liquid crystals have an intrinsic conductivity which exceeds by 6–8 orders of magnitude the impurity conductivity in classical organic liquid crystals. Data obtained by Meisel et al.[18] indicate that the charge transfer in the carboxylate melts is effected mainly by metal cations.

The structure of the mesophases of ionic liquid crystals has been investigated by X-ray diffraction, ^1H NMR, and ^{23}Na NMR for sodium butyrate and isovalerate[19-21] and by X-ray diffraction for potassium caproate (hypotheses concerning the structure were put forward on the basis of X-ray diffraction studies on single crystals[22]) and thallium and sodium n-alkanoates.[23-25] It has recently been possible to investigate a series of crystal structures of such salts and this yielded more refined and detailed information about the structure of the mesophases.

There have been few structural studies on the single crystals and thermotropic mesophases of metal alkanoates and complete X-ray diffraction analysis has been achieved mainly for certain hydrated formates and acetates.[26] The reason for this is the difficulty of obtaining single crystals of salts of this group. However, reports have recently appeared concerning structural studies on such salts, in particular barium butyrate ($BaBut_2$), which forms a smectic phase A:

$$\text{Crystal (C)} \xrightarrow{240\ ^\circ C} \text{smectic phase (SmA)} \xrightarrow{304\ ^\circ C} \text{isotropic liquid (IL).}$$

This compound was synthesised by the method described by Hazlewood et al.[27]

The crystal structure of $BaBut_2$ contains two symmetrically independent barium atoms, each of which is coordinated to eight oxygen atoms.[28] The coordination of the barium atoms can be described in terms of a polyhedron, the lower and upper bases of

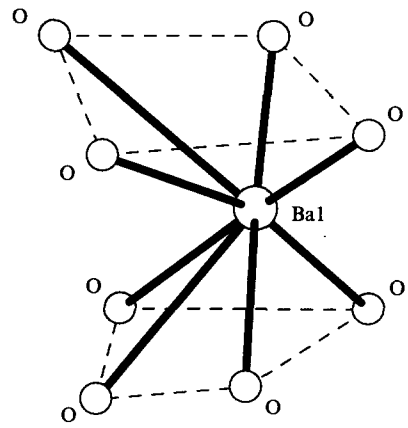


Figure 1. Coordination of the Ba(1) atom in the $BaBut_2$ structure.[28] The angle between the planes formed by the oxygen atoms is 9°.

which comprise irregular rectangles rotated relative to one another (Fig. 1). In this coordination, the barium atom is, as it were, compressed by two 'oxygen lids', on either side of which the alkyl chains of the butyrate anions are disposed. The metal–oxygen bonds are significantly ionic (the sum of the ionic radii is less than or equal to the Ba–O distances found in the crystal: 2.687–2.936 Å). It should be especially noted that Mirnaya et al.[28] established for the first time the disposition of the metal cations and the carboxylate groups of the anions for ionic liquid crystals. Since the type of packing of the molecules in the mesogenic crystal can be to some extent inherited by the mesophase, the observed coordination of the metal should be retained, at least in broad outline, also in the mesophase, as has been observed, for example, for metal complexes of Schiff bases and a number of other compounds.[5,6,8] The packing of the molecules in the $BaBut_2$ crystal has an explicit bilayer character and within each double layer hundreds of barium and oxygen atoms form electrically charged cation–anion strata separated from one another by layers of alkyl substituents (Fig. 2). One may postulate that during fusion the 'acceleration' of the alkyl substituents occurs before the breakdown of the barium–oxygen strata. As a result, the sliding of the alkyl layers relative to one another becomes possible, which favours the formation of the smectic mesophase.

Low angle scattering studies on the vitrified $BaBut_2$ mesophase showed[28] that the thickness of the bilayer (14.02 Å) is somewhat smaller than that of the corresponding bilayer in the crystal (14.63 Å). This may be associated with the partial compression of the layers in the mesophase due to the strong electrostatic interactions between neighbouring bilayers. The same effect has been observed also for homologues of thallium n-alkanoates,[29] where there are considerable possibilities for conformational changes in the alkyl chains. The addition of different amounts of sodium butyrate (20, 40, and 50 mol%) to the $BaBut_2$ melt hardly alters the interlayer distance in the mesophase. This can be explained by the similar polarising capacities of both cations and also by the fact that the changes in composition indicated do not entail appreciable changes in the nature of the electrostatic interactions in the cation–anion stratum and hence in the bulk of the stratum.

The smectic mesophase A has been observed[30] also for the hydrated form of cadmium isovalerate, the structure of which is in broad outline similar to that of $BaBut_2$.

$$\text{C} \xrightarrow{180\ ^\circ C} \text{SmA} \xrightarrow{237\ ^\circ C} \text{IL}$$

The metal atom in the crystal occupies a specific position on the twofold axis and is coordinated to six oxygen atoms, two of which belong to water molecules. The coordination environment of the

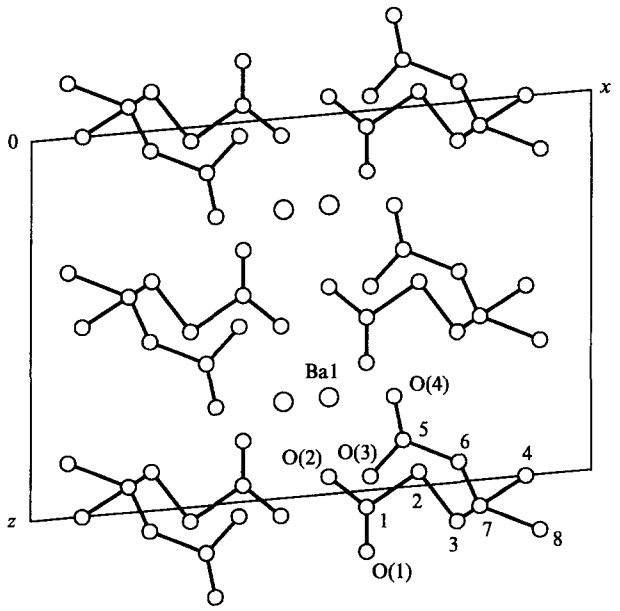


Figure 2. The packing of the first independent barium butyrate molecule in projection onto the *xz* plane.

cadmium atom is represented by a polyhedron, the lower and upper bases of which comprise triangles made up of oxygen atoms and linked by a twofold crystallographic axis. The angle between them is 14.8°. The disposition of the molecules in the cadmium complex is of the double layer type, as in the $BaBut_2$ crystal: the cadmium and oxygen atoms form strata between which the alkyl chains are accommodated. The presence in the structure of two water molecules leads to the formation of two chains of hydrogen bonds which join together the anions within one bilayer.

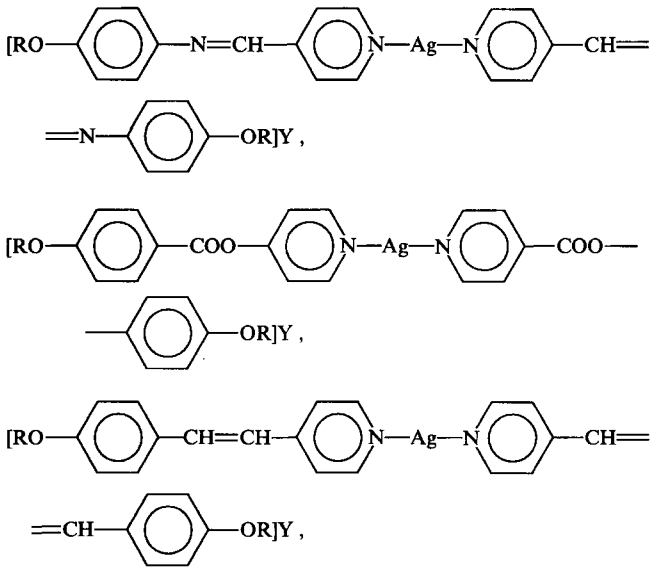
The thickness of the bilayers in the mesophase (14.1 Å) exceeds appreciably the thickness of the layers in the crystal (12.29 Å). This can be explained by the inclined disposition of the molecules in the crystal relative to the plane of the layer, which changes to an orthogonal disposition on passing to the smectic phase A. IR spectroscopic studies have shown that, when crystals of cadmium isovalerate are heated and pass to the mesophase, there is only partial loss of water, the presence of which is responsible for the mesomorphism (the anhydrous substance does not form the mesophase).[30]

The absence of mesomorphism in magnesium butyrate hydrate ($MgBut_2.4H_2O$), the crystal structure of which is also characterised by a bilayer disposition of the molecules,[30] can be attributed to the high polarising capacity of the cation, as a result of which the condition for the existence of ionic liquid crystals, namely $Z_k/r_k^2 < 1.05$ (Z_k and r_k are respectively the charge and radius of the cation) is not fulfilled because of the small radius of the metal.[31] However, we believe that the presence in the crystal of a branched three-dimensional network of hydrogen bonds is also unfavourable for the manifestation of mesomorphism. Furthermore, water molecules shield the Mg^{2+} cation in such a way that the second butyrate anion is not linked directly to the metal cation. The presence of such a bond is apparently essential for the formation of ionic liquid crystals.

It is noteworthy that ionic liquid crystals and their binary mixtures are promising materials for the preparation of supercooled mesomorphic substances—liquid-crystal glasses. Furthermore, ionic liquid crystals exhibit a high optical sensitivity, which can be varied by the application of even weak electric fields.

2. Salts of complex cations

Silver salts with complex cations and various anions constitute a fairly numerous group of ionic liquid crystals:[32, 34]



where $Y = BF_4^-$, NO_3^-, $CF_3SO_3^-$, or $C_{12}H_{25}SO_4^-$ and $R = C_nH_{2n+1}$. Wider ranges of conditions for the existence of mesophases and a greater variety of polymorphic modifications than for salts with imino-ligands are characteristic of salts with ester ligands in this group. The greatest number of mesomorphic phases has been observed for salts with stilbazole ligands and the dodecyl sulphate anion (DOS), this being particularly notable for the alkoxy-homologues with $n > 5$.

Fig. 3 presents the phase diagram for the homologues of the last of the salts listed above [derivatives of *trans*-4-alkoxy-4′-stilbazole (TAS)]. The columns on the diagram correspond to phase transitions investigated by differential scanning calorimetry and X-ray diffraction, including the procedure using synchrotron radiation. For example, on the X-ray diffraction pattern for the $[Ag(TAS)_2][DOS]$ ($R = C_3H_7$) nematic phase, a peak was found corresponding to a distance of 33.1 Å, in good agreement with the length of the complex anion, which is 35.1 Å. For the homologue with $R = C_{12}H_{25}$, the phase at 138 °C was identified as cubic with a unit cell parameter of 73.4 Å. This isotropic cubic phase (M_I on the phase transitions scheme—see Fig. 3) proved to be similar to the phase D found earlier for biphenylcarboxylic acids.[35] The properties of salts with other anions (NO_3^-, $CF_3SO_3^-$) are close to

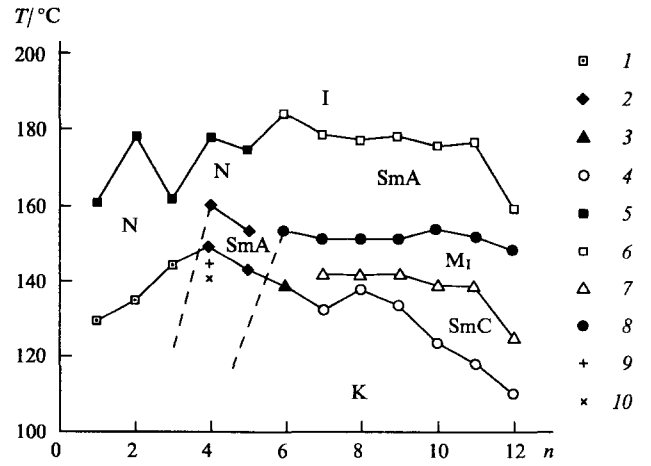


Figure 3. Phase diagram for the $[Ag(TAS)_2][DOS]$ homologues.[34] The region of existence of the SmA phase is indicated by dashed lines. Phase transitions: (*1*) C → N; (*2*) C → SmA and SmA → N; (*3*) C → M_I; (*4*) C → SmC; (*5*) N → I; (*6*) SmA → I; (*7*) SmC → M_I; (*8*) M_I → SmA; (*9*) SmA → N_R; (*10*) N_R → SmC; N = nematic phase, N_R = reverse nematic phase; C = crystal; I = isotropic liquid.

those found for the DOS salts, but they do not form so many polymorphic phases. The pronounced poly-morphism of the silver salts examined may find applications in electrochemistry.

III. Liquid-crystal coordination compounds

At the present time coordination compounds constitute the most numerous group of metal-containing liquid-crystal substances which has also been investigated in greatest detail. Their behaviour is similar to that of classical organic liquid crystals, since, in contrast to ionic liquid crystals, they represent molecular phases. However, the presence of a metal naturally gives rise to a series of new properties.

In this section we shall consider complexes with carboxylate, β-diketonate, salicylaldiminate, and other ligands, the majority of which are also mesogenic compounds in the noncoordinated state. Comparison of the structures of the mesophases of the coordination compounds and the free ligands is of interest in many instances since it makes it possible to predict the trend in the variation of the properties of these compounds.

1. Complex mesogenic substances with carboxylate ligands

Copper stearate was the first to be investigated among the mesogenic carboxylates.[36] The method of synthesis, the structures of the solid and liquid crystal phases, and the mobilities of the molecules of the above compound and other carboxylates of the type $M_2(\mu\text{-}O_2CC_nH_{2n+1})_4$, where $n > 4$ and M = Cu, Ru, Rh, or Mo, have been investigated by many workers.

Divalent metal carboxylates are usually obtained by the exchange reactions between alkali metal salts of aliphatic acids and the salts of the corresponding divalent metals. Furthermore, it is possible to obtain them by fusing aliphatic acids together with metal hydroxides.[37] The molecular structure of the carboxylates is fairly well known[38-40] on the basis of X-ray diffraction data for single crystals of copper alkanoates with n = 4, 8, and 10. Their molecules are dinuclear complexes in which each copper atom is involved in a square-bipyramidal coordination and is surrounded by four oxygen atoms in the equatorial plane. One of the vertices of the pyramid is occupied by the copper atom and another is occupied by an oxygen atom of a neighbouring complex (Fig. 4). The average Cu–O distance for all five oxygen atoms is 2.01 Å and the Cu–Cu distance is 2.59 Å. The molecules in the crystals of the alkanoates investigated are packed in stacks in such a way that the axis of the stack passes through the centres of gravity of the molecules.

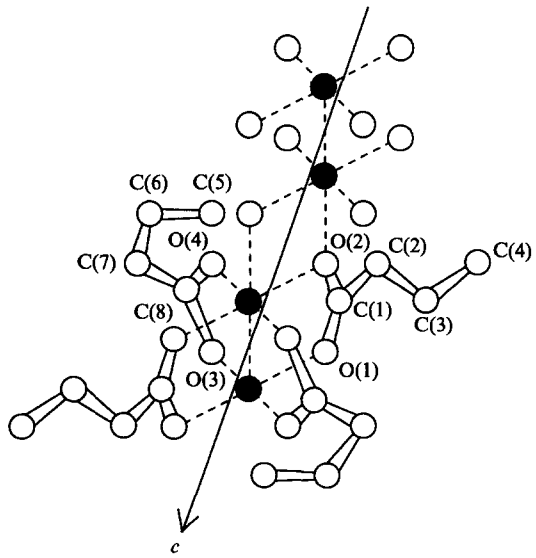


Figure 4. The structure of the copper carboxylate complex (n = 4) in the crystal.[38] The arrow indicates the direction of the column.

Systematic studies have been made[41-45] on copper carboxylates with n = 4–24 by differential scanning calorimetry, optical microscopy, X-ray diffraction of the mesophase, and EXAFS spectroscopy. X-Ray diffraction study of the mesophase showed[45] that, at temperatures above 120 °C, copper carboxylates form a columnar discotic phase with a planar hexagonal lattice. In the mesophases investigated, the nuclei of the dinuclear complexes are arranged along the axis of the column and, regardless of the length of the alkyl chains, the distance between the neighbouring complexes in the column is 4.7 Å. The distances between the columns themselves vary as a function of the length of the alkyl chains and amount to 15–25 Å. We may note that the disposition of the molecules in the mesophases considered (Fig. 5) and in the single crystals of these compounds is similar. It is believed[42] that the mesophases of the copper carboxylates are the first example of a thermotropic columnar liquid crystal phase in which the molecules with four equivalent substituents (the intrinsic symmetry of the molecule approaches the quaternary symmetry) form a hexagonal phase. EXAFS spectroscopic data confirmed that the metal–metal distance in the dinuclear complex remains unchanged when the crystal passes to the mesomorphic state.[43]

The carboxylate complexes of tetrakis[2,2-(dioctyl)acetate-*O*,*O*′]dicopper(II) have been investigated.[46] A distinctive feature of these complexes with branched substituents is the fact that the temperature of the range corresponding to the existence of the mesophase is reduced below room temperature and reaches −20 °C. It may be that, apart from the chain branching, this is influenced also by the presence of impurity ions in the mesophase. X-Ray diffraction study made it possible to assign this mesophase to the discotic columnar hexagonal type with distances of 4.6 Å between the discs and 21.5 Å between the columns. Molecular complexes between the above copper carboxylate and pyrazine and 4,4′-bipyridyl also form mesophases, the structure of which has not yet been established unambiguously.

A similarity in the behaviour and structure has been noted for divalent rhodium carboxylates and the analogous copper complexes.[47] According to EXAFS spectroscopic data, the Rh–Rh distance in the dimeric complex $Rh_2(\mu\text{-}O_2CC_7H_{15})_4$ is 2.38 Å, while the intermolecular distance Rh...Rh, which completes the coordination of the metal atom, is 3.16 Å. The presence of the additional coordination in the mesophase has been confirmed also by Raman spectroscopic data.[48] This suggested that the authors dealt in this instance for the first time with a columnar type complex in which there is a chain of metal–metal bonds within the discotic column. Mesophases with a similar structure have been observed also for dinuclear chromium and molybdenum complexes,[49,50] in the latter case the metal atoms being linked by a quadruple bond. Similar phases have been found for dinuclear ruthenium(II) complexes. The synthesis and properties of the mixed valence ruthenium complexes $Ru(RCO_2)_4X$, where R = C_8H_{17} or $C_{11}H_{23}$ and X = Cl or RCOO, have been described.[51] It was found that the complexes with X = Cl are nonmesogenic, while those with X = RCOO form hexagonal (R = $C_{11}H_{23}$) or orthogonal (R = C_8H_{17}) columnar mesophases.

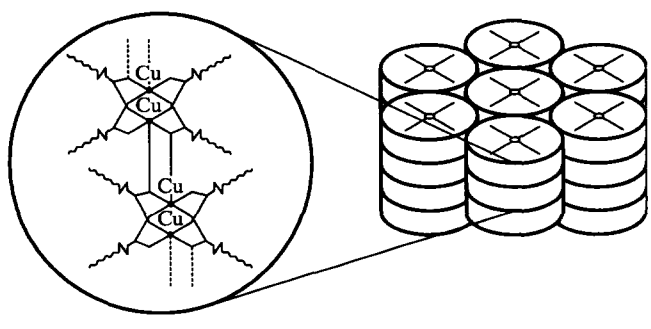
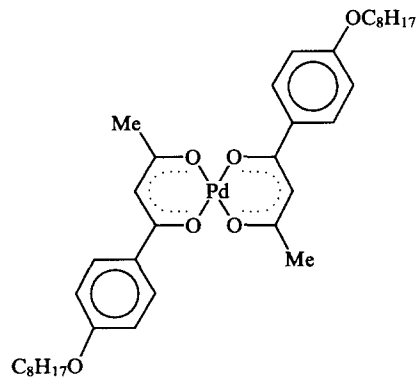


Figure 5. The columnar mesophase of copper carboxylates.[7]

These compounds are apparently the first example of liquid crystals with a mixed valence.

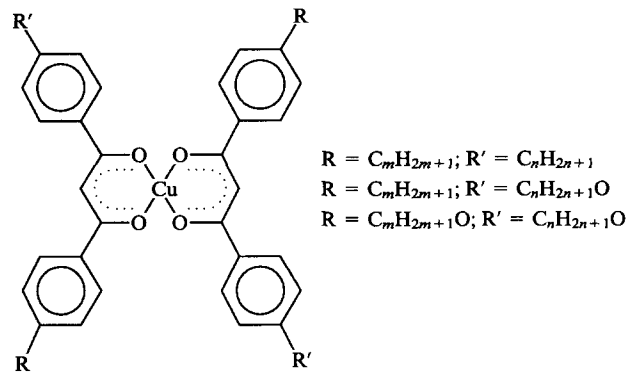
2. Mesogenic complexes of β-diketonates

The diligand complexes of β-diketones, especially those with palladium and copper having suitable substituents, exhibit mesomorphic properties in many cases. These complexes can be obtained by the reaction of β-diketones with the salts of the corresponding metals. Mesomorphism was first observed and described[52] for the palladium complex, the molecule of which is rod-shaped.



It has been stated[52] that, although the above complexes exhibit mesomorphism (according to differential scanning calorimetric data), it has not been possible to investigate it by optical methods owing to the darkening of the specimens on heating. The analogous copper complexes with alkyl substituents of different lengths do not exhibit mesomorphism.[53]

The copper complexes, first described by Giroud-Godquin and Billard,[54,55] in which the β-diketonate ligands each have two phenyl groups with the same or different terminal substituents in the *para*-position, are assumed to be much more promising mesogenic substances.



Complexes of this type tend to form highly ordered discotic, especially layered, phases. The complexes of β-diketonates with identical alkyl substituents at the phenyl groups have higher melting points and clarification temperatures than the same complexes with different substituents. For example, the range of existence of the mesophase is 71–122 °C for $n = 7$ and $m = 13$, 89.5–128.5 °C for $n = m = 10$, and 95.1–113.4 °C for $n = m = 12$. It has been established[7] that the region corresponding to the existence of the mesophase is wider for complexes with terminal alkyl substituents than for complexes with alkoxy-substituents. On the other hand, the analogous nickel diketonate complexes do not form mesophases at all.[55]

The structures of the single crystals of two complexes of this series with R = R' = $C_8H_{17}O$ and R = R' = C_8H_{17} have been established.[56–58] We may note that hitherto this has been achieved only for very few compounds forming discotic phases. According to X-ray diffraction data, the copper atom has a square planar configuration and the angle of rotation of the benzene rings relative to the plane of the central nucleus does not exceed 20°. As in other mesogenic molecules,[5,8] the alkyl chains are characterised by high thermal factors, indicating their appreciable mobility, which decreases even further in the mesophase.

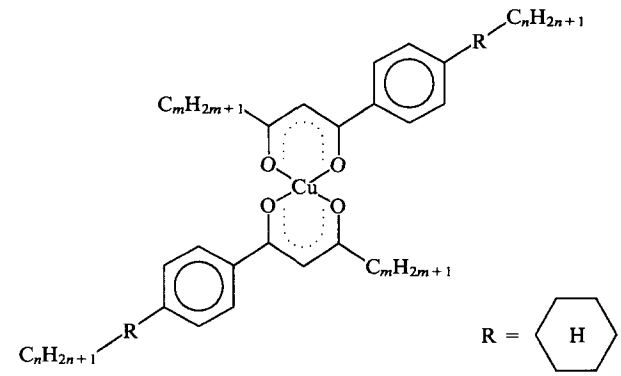
The packing of the molecules in the crystal with R = OC_8H_{17} is of the layered-columnar type.[57] In contrast to the usual discotic phases, the molecules in the column are grouped into centrosymmetric dimers and each column is surrounded by six neighbouring columns, but their relative disposition is far from being of the hexagonal type. The central part of the column is surrounded on all sides by alkyl substituents belonging to the given column and neighbouring columns (Fig. 6).

The columnar arrangement is not, however, characteristic of all compounds of this series. Thus X-ray diffraction data for the mesophase of molecules with R = R' = $C_{12}H_{25}$[59] made it possible to attribute to it a layered structure with a uniform distribution of molecules in the layer and without a columnar ordered arrangement.

It has been shown[60,61] that an increase in the number of substituents in the benzene rings of 1,3-diphenyl-β-diketones also makes it possible in a number of instances to obtain discotic compounds. Discotic phases have been observed for phenyl-substituted copper complexes with hydroxyalkyl substituents in the 3- and 4-positions, but have not been found for 3,5-diphenyl-substituted complexes. The analogous nickel complexes do not form mesophases. Mesophases have also not been observed for a number of other complexes with alkyl substituents.[62]

In the presence of substituents in the benzene rings, imparting to the β-diketone compounds a significant anisometry (for example in the case of copper complexes[63,64] with R = Ar-$C_{10}H_{21}$ and R' = Me, Et, OMe, OEt, or OPr), the type of the mesophase formed changes. It becomes nematic, retaining at the same time features characteristic of discotic nematic phases. It is believed[65] that this group of compounds is the first example of biaxial nematic metallomesogenic substances.

Similar complexes with one phenyl and one alkyl substituent in the β-diketone ligand also form nematic phases.[66]



It has been possible to investigate the crystal structures of two of them with $n = 3$ and $m = 1$, and with $n = 3$ and $m = 8$.[66] The structure of the first molecule is nearly planar (with the exception of a slight rotation of the benzene rings, by not more than 12°, relative to the plane of the metal chelate ring). On the other hand, the second molecule is significantly nonplanar: not only the benzene rings have been displaced from the central plane (by not more than 21°) but also the alkyl substituent (by ~40°). Evidently, the compound constructed from rod-shaped molecules with $n = 3$ and $m = 1$ exhibits nematic properties. The molecules with $n = 3$ and $m = 8$ are packed in the crystal in layers, which indicates the possibility of the existence of the smectic phase. However, the compound forms only a monotropic nematic phase. In our view, this can be explained precisely by the presence in the crystal of layers, which must be disrupted to achieve the transition to the nematic phase directly from the solid phase. Apparently such disrupting effect on the layered structure

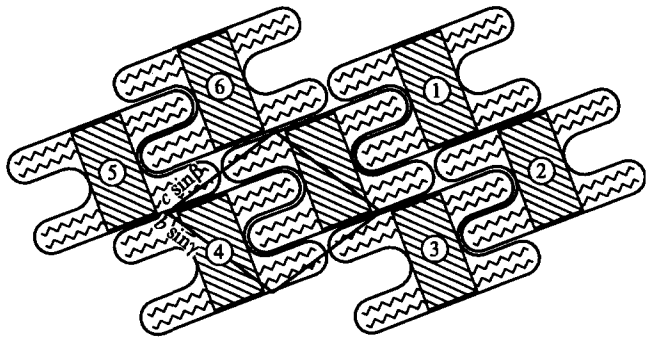
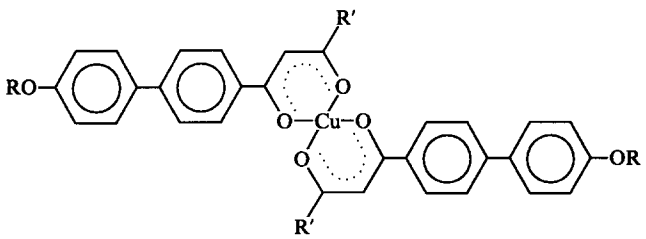


Figure 6. Columns in the crystal[57] of a copper β-diketonate complex (R = OC_8H_{17}). The dimers are surrounded by a continuous line and their central parts are shaded. The numerals denote the nearest neighbours of the dimer.

is exerted by the added 4-cyano-4′-(4″-*n*-pentylcyclohexyl)-biphenyl. The reason for the absence of the smectic phase can be found by analysing the energy of the intermolecular interaction, for example by the method used by Polishchuk et al.[8]

At first sight it is entirely natural to postulate, on the basis of the shape of the molecule, the presence of a nematic mesogenic phase for compounds having the general formula



the synthesis, properties, and structure of which have been described in the case of homologues with R′ = Me, R = C_nH_{2n+1}, and n = 8–12, 16, or 18.[67]

All the homologues indicated, except that with n = 8, form the so called orthogonal columnar ordered discotic mesophase D_{ho}, which had not been mentioned initially in the classification of discotic mesophases proposed by Destrade et al.,[68] but which has been recently added to this classification.[69] The mesophase of the homologue with n = 16 has been studied in greatest detail by X-ray diffraction. The results made it possible to construct a model of the mesophase (Fig. 7). The molecules of this homologue are rod-shaped and not disc-shaped and the authors therefore assume that the elementary units from which the columns are made up are molecular dimers. Similar dimers had been detected also previously in the crystal structures of discotic substances, in particular in the complexes, mentioned above, described by Usha et al.[56] and Muhlberger and Haase.[66] The dimers (Fig. 7*a*) are arranged in an ordered fashion along the column axis (Fig. 7*b*). The disposition of the columns is characterised by a planar orthogonal lattice $C2/m$ symmetry having the parameters indicated in Fig. 7*c*. This example confirms yet again that not only the shape of the molecule but also the nature of their aggregation within the mesophase is important for the formation of a columnar discotic phase. In our view, however, this phase should not be referred to as discotic, since it contains no disc-shaped molecules and should probably be assigned to the class of phases made up of columnar associated nondiscotic molecules, for example, of the kind described by Polishchuk and coworkers.[5,6]

As a result of the introduction into the above complexes of more bulky substituents R′, for example, C_4H_9, C_8H_{17}, and $C_{12}H_{25}$, the molecules become less anisometric and cease to form discotic phases of type D_{ho}, forming instead enantiotropic or

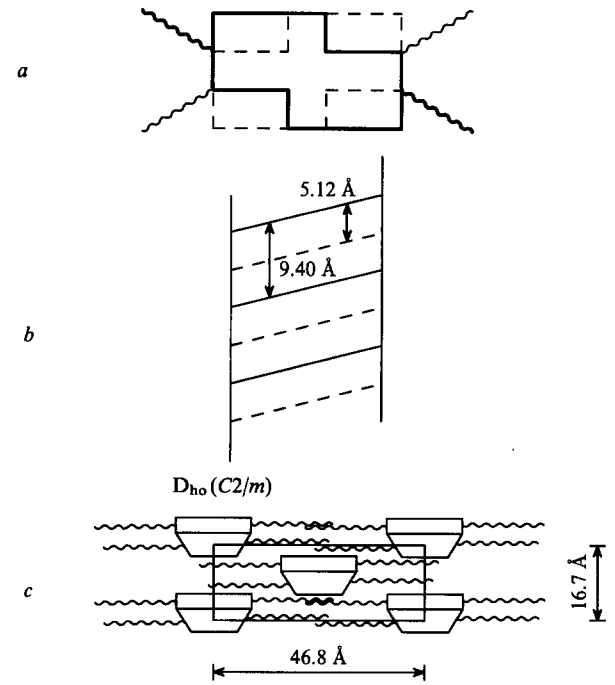


Figure 7. 'Discotic' phase made up of rod-shaped molecules:[67] (*a*) schematic illustration of the structure of the molecular dimer; (*b*) disposition of the dimers in stacks (interdimer distance 9.40 Å, intradimer distance 5.12 Å); (*c*) schematic illustration of the packing of the columns in the orthogonal mesophase — the parallelopipeds represent the central parts of the molecular dimers.

monotropic nematic phases.[70] The phase transitions in these compounds are illustrated schematically in Table 1. The nature of the nematic mesophase is determined by the ratio of the lengths of the substituents R and R′, i.e. by the shape of the molecule. The replacement of the small methyl groups (Fig. 8*a*) by the more bulky n-butyl groups (Fig. 8*b*) prevents the formation of the discotic phase D_{ho} and, on still further increase in their length and hence in the mobility and disorder of the terminal alkyl substituents, the nematic phase can be obtained only from the isotropic liquid on rapid cooling. After prolonged maintenance of the melt at a temperature several degrees below the clarification temperature, the formation of helicoidal mesophases was

Table 1. Phase transition temperatures (°C) in nematic copper β-diketonate complexes.

R	R′	Phase transition
C_4H_9	C_4H_9	C $\xleftrightarrow{201.0}$ N $\xleftrightarrow{205.3}$ IL
C_8H_{17}	C_4H_9	C $\xleftrightarrow{170.0}$ N $\xleftrightarrow{176.3}$ IL
$C_{12}H_{25}$	C_4H_9	C $\xleftrightarrow{111.5}$ C_2 $\xleftrightarrow[\text{slow}]{153.3}$ IL; C_2 $\xrightarrow[\text{fast}]{}$ N $\xrightarrow{}$ IL
C_8H_{17}	C_8H_{17}	C $\xleftrightarrow[\text{slow}]{166.9}$ IL; C $\xrightarrow[\text{fast}]{155}$ N $\xrightarrow{}$ IL
$C_{12}H_{25}$	$C_{12}H_{25}$	C_1 $\xrightarrow{108.5}$ C_2 $\xrightarrow{128.5}$ C_3 $\xrightarrow{139.5}$ IL; C_4 $\xleftrightarrow[\text{slow}]{147.5}$ IL; C_4 $\xrightarrow[\text{fast}]{137.0}$ N $\xrightarrow{}$ IL

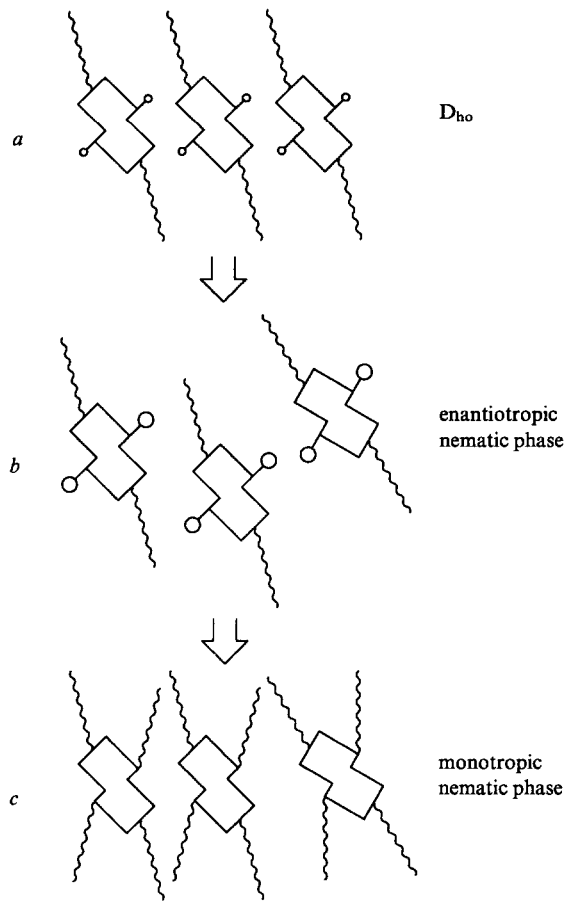
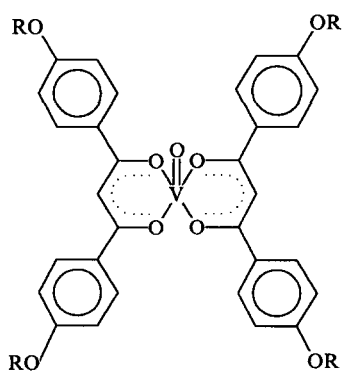


Figure 8. Three types of molecules forming the 'discotic' (*a*), enantiotropic (*b*), and monotropic (*c*) nematic phases.[70]

observed for compounds exhibiting monotropic nematic mesomorphism (Fig. 8*c*). It is of interest that the corresponding noncoordinated ligands form smectic phases.[70]

Nematic mesophases of the enantiotropic or monotropic types[71] (except for one case where a smectic mesophase was found) have also been observed for a large number of similar complexes in which one of the phenyl rings has been replaced by a cyclohexyl or fluorophenyl ring.[71] In contrast to the previous group of complexes, here the mesomorphism of the ligands themselves is more varied. Nematic phases and smectic mesophases of different types have been observed for such ligands.

So far few mesogenic complexes of other metals with β-diketonate ligands have been found. One may mention the octahedral complex of trivalent iron[7] $Fe(RCOCHCOR)_3$, which

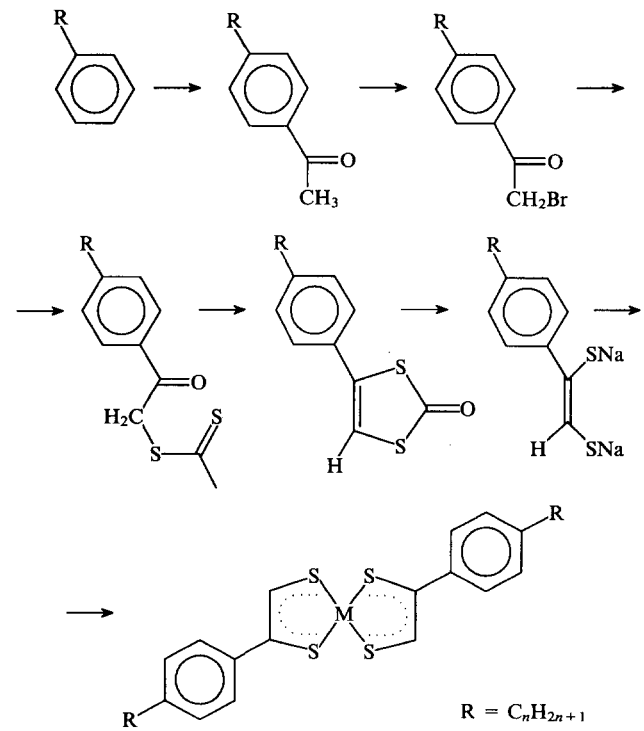


R = $C_{10}H_{21}O$

is apparently the first example of an octahedral metallomesogenic substance, and mesogenic oxovanadium(IV) complexes[72] for which discotic hexagonal columnar phases D_h have been found.

3. Mesogenic dithiol metal complexes

Dithiol complexes have structures similar to those of carboxylate complexes and, depending on the nature of the terminal substituents, it is possible to observe nematic, smectic, or discotic phases for such compounds. We shall describe the first series of dithiols, one of the most thoroughly investigated, which have been synthesised in accordance with the following scheme.[73-76]



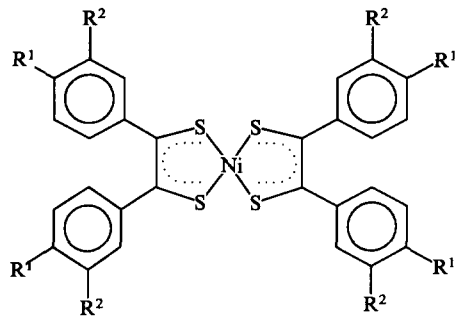
R = C_nH_{2n+1}

The above complexes (M = Ni, Pt)[75] exhibit nematic mesomorphism for n = 4 and 5 and form the SmA phase when $n \geqslant 6$.

A structural study on a single crystal of the nickel complex (n = 8) showed[76] that the coordination of the metal atom is planar and the substituents are distributed in the *trans*-orientation, which is the reason why the molecule has the shape extended to the maximum degree. The molecules in the crystal are packed in layers, which is apparently a precondition for the manifestation by these compounds of smectic mesomorphism.

It has been suggested that the molecules of dithiol complexes, having appreciable electron-accepting properties, can form charge-transfer complexes (CTC) with electron-donating molecules, for example, with liquid-crystal derivatives of tetrathiofulvalene.[77] However, it has been found that the compounds synthesised do not form charge-transfer complexes.[77] On the other hand, they can be used in a mixture with cyanobiphenyls as laser dyes.[78] Finally, it has been noted[75] that palladium complexes do not exhibit the properties of liquid crystals for the entire series of homologues, in contrast to the analogous nickel and platinum complexes. The authors believe that the reason for this difference is the dimerisation of the palladium complexes as a result of the metal–metal interaction, which predominates over the dispersion forces.

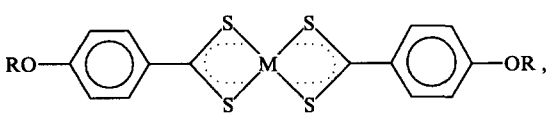
Complexes with two phenyl substituents in each dithiol ligand, whose structure is similar to that of the diphenyl-substituted β-diketonates, also exhibit discotic mesomorphism, the type of mesophases being different for complexes with monosubstituted and disubstituted phenyl groups.



For the monosubstituted phenyl derivatives with four substituents $R^1 = p\text{-}C_nH_{2n+1}$ ($n = 8-12$), $R^2 = H$ and $R^1 = p\text{-}C_nH_{2n+1}O$ ($n = 7-12$), $R^2 = H$, the formation of only layered discotic phases has been established.[79,80] The search for columnar phases in compounds of the above type has continued, since these compounds could have interesting electrochemical properties. It has been observed[81] that the introduction of two alkyl substituents $R^1 = R^2 = p\text{-}C_nH_{2n+1}$ ($n = 6, 8$) does not lead to the formation of a mesophase at all, while the compound with the alkoxy-substituents $R^1 = R^2 = p\text{-}C_{10}H_{21}O$ forms a hexagonal phase D_{hd} with disordered columns (the hexagonal lattice parameter is 32.7 Å and the distance between the mobile alkyl chains is 4.4 Å). Subsequently the entire series of complexes with $R^1 = R^2 = p\text{-}C_nH_{2n+1}O$ ($n = 1-12$) was investigated systematically.[82] It was found that all the complexes with $n \geqslant 5$ form enantiotropic discotic phases D_{hd}, while the first members of the series ($n = 2-4$) form monotropic discotic phases. The half-wave potential for the reduction of these complexes is independent of the length of the substituents and its values are close to −0.05 to 0.06 V. This is somewhat smaller than the value for the unsubstituted complex, which indicates the independence of the electrochemical properties of the mesogenic nature of the specimens.

4. Metal dithiocarboxylate complexes

By analogy with metal carboxylates, it was natural to expect the manifestation of mesogenic activity by thiocarboxylates. Their synthesis and study by differential scanning calorimetry and X-ray diffraction[83] did indeed confirm the validity of such hypotheses. The mesogenic properties of the complexes $M(C_nH_{2n+1}OC_6H_4CS_2)_2$,



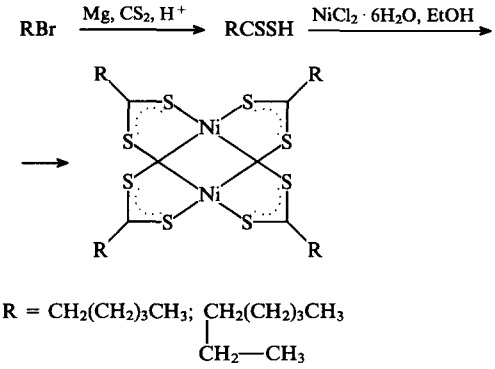
where M = Zn, Ni, or Pd and $n = 4-10$, were investigated.

An analogous mercury complex, described by Adams et al.,[83] has also been mentioned.[7] The replacement of the metal in the complex leads to the appearance of different types of mesophases. For example, for $n = 8$ the zinc complex forms only nematic phases, whereas the palladium and nickel complexes give rise to several smectic phases in addition to the nematic phases. This may be associated with the different types of coordination of the metal in these complexes. Thus a tetrahedral coordination is usually characteristic of zinc, although in the case of the complex with $n = 4$ dimers were found in the crystal in which the eight-membered ring Zn–S–C–S–Zn–S–C–S is present. In the crystal of the planar palladium complex, the metal atoms are involved in an additional coordination as a result of the interaction with the sulfur atoms of neighbouring molecules (the intramolecular Pd–S distances are 2.29–2.35 Å and the intermolecular Pd ... S distances are 3.38 Å). A similar molecular packing was found also in the mercury complex: the Hg–S distances within the complex are significantly nonequivalent, amounting to 2.41 and 2.96 Å, while the lengths of the Hg ... S intermolecular contacts are 3.36 Å.

It has been stated[84] that the palladium and nickel complexes exhibit a significant dichroism: after the passage of light along the molecular axes, the extinction coefficient is appreciably higher than in the case where light is transmitted at right angles. This property may be used to devise displays of the 'guest–host' type. For example, the nickel complex can serve as the guest in the cell, while the host is an organic liquid-crystal compound. If the molecules are oriented at right angles to the direction of light in the absence of an electric field and parallel to this direction in the presence of the field, then in the former case the cell is coloured purple while in the latter it is transparent.

Gold(III) alkoxydithiobenzoate complexes $ROC_6H_4CS_2AuCl_2$, forming SmA phases on heating, have been investigated.[84]

Apart from the nickel(II) bisthiocarboxylate complexes, the synthesis and properties of nickel(II) tetrakisdithiocarboxylate complexes have been described.[84,85]



Two series of tetrakis-complexes with linear and branched alkyl substituents were obtained.

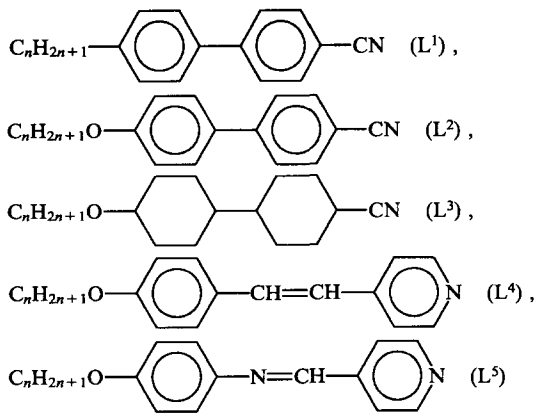
The results of differential scanning calorimetric and X-ray diffraction studies have shown that complexes with linear chains form monotropic lamellar (layered) discotic phases of the type D_l, whereas the presence of an enantiotropic discotic phase with a hexagonal columnar ordered arrangement of the type D_{hd} is characteristic of complexes with a branched alkyl chain. On heating of the given substance or on its dissolution in chloroform, the tetrakis-complexes are converted into the bis-complexes.

5. Mesogenic metal complexes with monodentate nitrogen-containing ligands

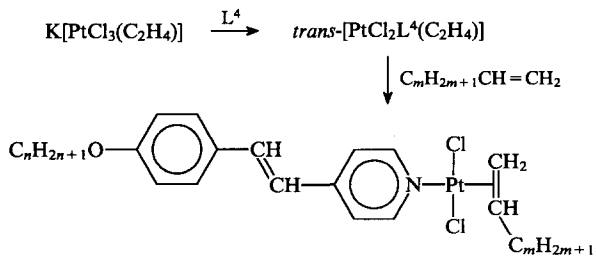
The widely known organic mesogenic substances, containing a nitrogen atom capable of forming a coordinate bond, can serve as monodentate ligands. Such mesogenic substances form metal complexes in reactions with platinum group metal halides or carbonyls. The complexes may contain one or two mesogenic ligands. Their properties have been thoroughly investigated. For example, the mesogenic properties of the free ligands and complexes with different metals have been compared.[7,86]

The majority of complexes of the type ML^2Cl_2 (M = Pt, Pd; $n < 9$) exhibit only nematic mesomorphism. With increase in chain length, smectic SmA and/or SmC phases are also observed.

The introduction into the complex of two different ligands, for example π-olefin and monostilbazole ligands, leads to an appreciable decrease in the temperature of the appearance of the mesophase. Such complexes were synthesised in accordance with the following scheme:[7]

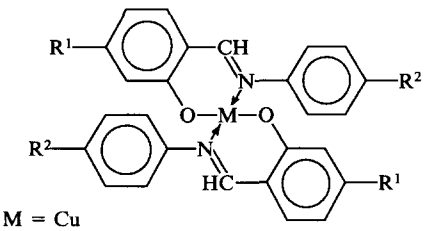


The presence of L^4 and L^5 ligands makes it possible to classify these complexes both as coordination and as organometallic compounds. The mesogenic properties of the complexes depend on the overall length of the alkyl chains of the two ligands. For $m+n < 8$, such complexes are nonmesogenic, forming a SmA phase with increase in chain length. They are monotropic for $m+n = 8-11$ and enantiotropic for $m+n > 11-13$.



6. Salicylideneamine metal complexes

The liquid-crystal properties of copper complexes of Schiff bases have been vigorously investigated in recent years. The synthesis of such compounds was first described by Ovchinnikov et al.[87] They obtained Schiff bases as a result of the interaction of 4-*n*-heptyloxy-2-hydroxybenzaldehyde with substituted anilines, after which the corresponding complexes were isolated by treating the bases obtained with copper acetate in ethanol.



M = Cu
$R^1 = OC_7H_{15}$
R^2 = H, F, CH_3, OC_nH_{2n+1} ($n = 1-8$)

In order to elucidate the influence of the nature of the metal atom on the mesomorphic properties, the analogous compounds with M = Zn, Co, Ni, Pd, and also VO were synthesised[88] ($R^1 = p$-OC_7H_{15}; $R^2 = p$-OC_8H_{17}). These compounds were obtained by refluxing in ethanol the corresponding metal acetate (potassium tetrachloropalladate was used for the palladium complex) with 4-heptyloxysalicylaldehyde and subsequent addition of 4-octyloxyaniline to the reaction mixture.

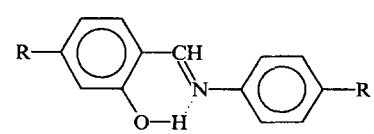
Studies by polarisation polythermal microscopy and differential scanning calorimetry showed that the substances obtained (Table 2) can be divided into two groups in terms of the nature of the phase transitions. The first includes copper, palladium, and vanadyl complexes, which have the properties of liquid crystals manifesting smectic or nematic mesomorphism. The second group includes cobalt, zinc, and nickel complexes, which in most cases do not form mesophases.

In order to establish the relation between the structure and liquid-crystal properties, single crystals of the metal complexes of the above series were investigated by X-ray diffraction, EPR spectroscopy, and electronic spectroscopy and also by the method involving low-angle X-ray scattering in the mesophase. Conformational calculations and calculations of the intermolecular interaction energy (IMIE) in the crystal were carried out on the basis of structural data.

In considering the complexes **1**–**13** in Table 2, we concentrated attention on the geometry of the metal chelate unit, because the ability of the metal complexes to exhibit mesomorphism is to a large extent determined by the coordination of the metal atom. Depending on the type of coordination of the metal, the molecules can assume a form with different degrees of anisometry, which plays a decisive role in the formation of the mesophase. Furthermore, as will be shown below, the liquid-crystal properties depend significantly on the possibility of the additional intermolecular coordination of the metal atom.

From the standpoint of understanding the causes responsible for the mesophase, compounds **1** and **2** proved to be the most important.[8,89] The crystal structures of these complexes are made up of two systems of symmetrically independent molecules with different coordinations of the copper atoms. In compound **1**, both molecules exist[8] in specific positions at the centre of symmetry and on the twofold axis (Fig. 9). The centrosymmetric molecules contain a copper atom involved in *trans*-square planar coordination, while the copper atom in the molecules on the twofold axis is involved in a tetrahedral coordination characterised by a dihedral angle of 60° (angle of twist) between the coordination planes of copper, nitrogen, and oxygen of the two ligands. In the structure of complex **2**,[89] one of the independent molecules is also located at the centre of symmetry, which predetermines the *trans*-square planar coordination of the metal, while the other occupies a general position with an approximate C_2 crystallographic symmetry and an angle of twist of 31°. A similar disposition of two independent molecules has been found[90] for the crystal of compound **3**, which is isostructural with compound **2**. The different coordinations of the copper atoms in the crystals of compounds **1**–**3** lead to different Cu–O and Cu–N bond lengths. For the tetrahedral coordination, these bonds are shorter, which is characteristic of complexes of the type considered.[100]

Comparison[8] of the conformations of the ligands in compound **1** with that of the similar noncoordinated nematogenic molecules of *p*-ethoxy-[101] and *p*-(n-propoxy)-salicylidene-*p*-(n-butyl)aniline[102] (ESBA and PSBA respectively) showed that the formation of the complexes does not entail significant changes in the conformation of the ligands. In particular, both in the complexes and in the noncoordinated molecules the benzene rings of the nitrogen atom have been significantly rotated relative to the chelate unit, while the benzene rings condensed with the unit are virtually coplanar with the latter (in ESBA and PSBA, the six-membered chelate ring, closed by a hydrogen bond, is entirely planar, while in the metal complexes the planar fragment of the chelate unit is made up of five nonmetal atoms). In both cases, the significant rotations of the benzene rings can be accounted for by intramolecular steric interactions.



R = OC_2H_5 (ESBA),
R = OC_3H_7 (PSBA),

Analysis of the configurations of the planar molecular complexes showed[95] that such molecules are incapable of forming the discotic mesophases postulated initially.[87] A discotic mesophase is not formed owing to the lack of an overall planar anisometry characteristic of it.[2] This is associated with the

Table 2. Phase transition temperatures (°C) and the type of coordination of the metal atoms in complexes of Schiff bases.

No.	M	R^1	R^2	N	SmC	SmA	Isotropic liquid	Coordination of metal	Ref.
1	Cu	OC_7H_{15}	OCH_3			132.9	140.0	Planar[d], tetrahedral	8
2	Cu	OC_7H_{15}	OC_5H_{11}		148.0	151.0	168.0	"	89
3	Cu	OC_7H_{15}	OC_6H_{13}		149.0	152.0	168.0	"	90
4	Co	OC_7H_{15}	OCH_3				137.0	Tetrahedral	91
5	Co	OC_3H_7	OC_7H_{15}				122.0	Octahedral	91
6[a]	Pd	OC_7H_{15}	OCH_3			203.0	226.0	Planar	92
7	Pd	OC_7H_{15}	OC_6H_{13}		158.3	171.0	180.0	"	93
8[b]	Ni	OC_7H_{15}	OCH_3				138.0 155.0	"	94
9	Cu	OC_7H_{15}	F			130.1	150.5	Square-pyramidal	95
10	Cu	OC_7H_{15}	CH_3				150.1	"	96
11	Cu	OC_7H_{15}	CN	(190)[c]			202.0	Square-bipyramidal	97
12	Cu	OC_7H_{15}	NO_2				220.0	"	98
13	Cu	H	$COOPhC_9H_{19}$	196.0			201.0	Planar	99

[a] A phase transition is observed in the crystal at 129 °C.
[b] Two melting points (see text).
[c] Temperature of the appearance of the monotropic nematic phase.
[d] Two independent molecules.

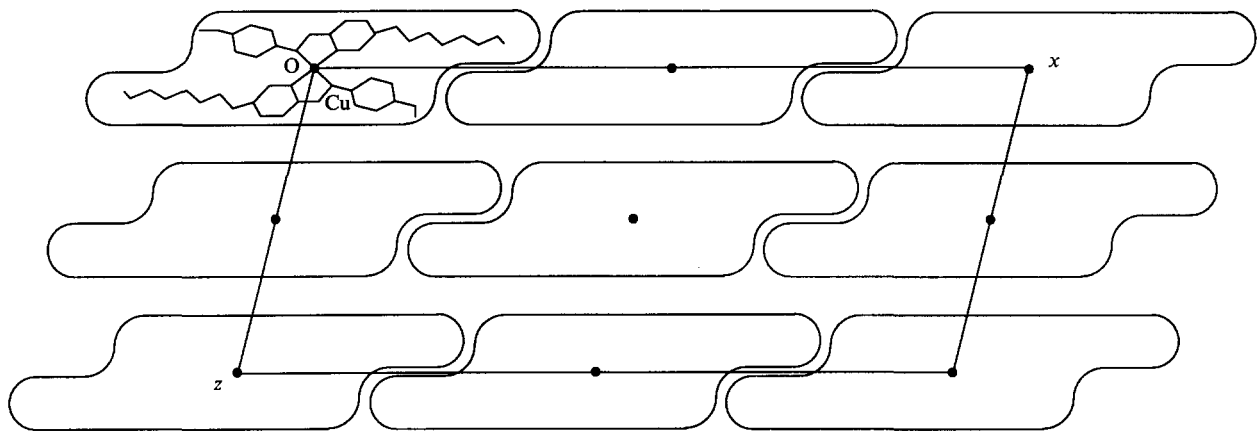


Figure 9. Arrangement of the molecules in the structure of a crystal of compound **1** located at the centres of symmetry. Individual molecules are involved in a projection – hollow type of arrangement. A similar type of packing is observed also for molecules located on twofold axes.[8]

rotation of the benzene rings[90] and with the stepped form of the coordination unit in molecules with the *trans*-square planar coordination of the metal atom.[95]

It was stressed for the first time[95] that, for the manifestation of mesomorphism, the square planar coordination is preferable to the tetrahedral coordination. Molecules with a *trans*-square planar coordination of the metal are characterised by a shape extended to the maximum extent by virtue of the parallel arrangement of the axes of the ligands (the angle of twist is 0°). On the other hand, the tetrahedral coordination leads to the rotation of the ligands relative to one another, which results in a decrease in the anisometry of the molecules. Thus the angle between the long axes of the ligands in the tetrahedral† molecules of compound **1** is[8] approximately 20°, but the most striking decrease in anisometry was manifested in a tetrahedral cobalt complex[91] (Table 2, compound **4**), in which the analogous angle of rotation is about 100° (Fig. 10). The absence of anisometry in the molecules has also been observed for an octahedral cobalt complex[91] (Table 2, compound **5**; Fig. 11).

†Here and subsequently in the text, the terms tetrahedral and planar molecules imply molecules with the corresponding coordination of the metal atom.

Thus the tetrahedral and octahedral coordinations of the cobalt atoms in complexes **4** and **5** actually preclude the formation of the mesophase in these compounds. The same causes

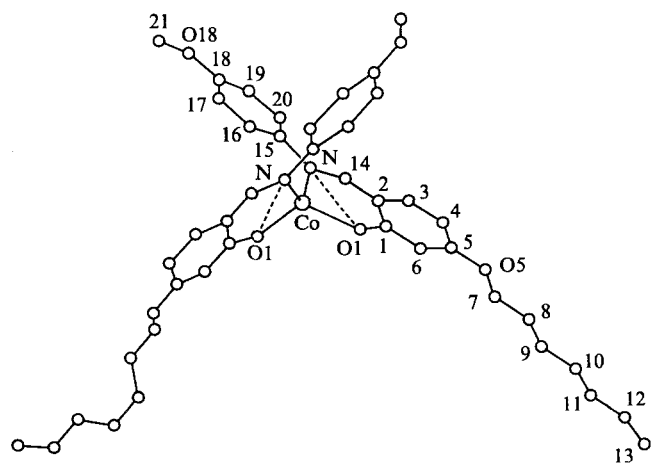


Figure 10. Molecular structure of a tetrahedral cobalt complex.[91]

apparently explain the absence of mesomorphism in zinc complexes with similar ligands as in complex **4**, because these compounds have the same structures.[91] An additional confirmation of the similarities of the structures of the zinc complexes and compound **4** is provided by the description[103] of the structure of a zinc complex of a Schiff base (R^1 = H; R^2 = CH_3), in which the metal atom has a tetrahedral coordination.

The presence in complexes **1**–**3** of two types of coordination of copper atoms indicates the conformational nonrigidity of the coordination metal unit. Therefore both planar and tetrahedral molecules may be present in the smectic phase.[8] This hypothesis was confirmed by the results of EPR studies. Bichkantaev et al.[104] investigated a single crystal of compound **1**, the EPR spectrum of which consists of a single Lorentzian line for all orientations of the crystal despite the presence of different types of complexes. The g-factors and their directions {g_1 = 2.2080, $\mathbf{n}_1$ = (0, 1, 0); g_2 = 2.0985, $\mathbf{n}_2$ = (0.866, 0, 0.5); g_3 = 2.0590, $\mathbf{n}_3$ = [$\mathbf{n}_1$, $\mathbf{n}_2$]} are inconsistent with the magnetic parameters of the individual complexes and are a result of the partial averaging of molecular g-factors due to spin exchange. The knowledge of the crystal structure of complex **1** made it possible to find the molecular magnetic parameters of each of the two types of complexes: $g_\perp^p \simeq 2.049$ and $g_\parallel^p \simeq 2.190$ ($g_o^p \simeq 2.096$) for the planar molecules and $g_\perp^t \simeq 2.068$ and $g_\parallel^t \simeq 2.298$ ($g_o^t \simeq 2.144$) for the tetrahedral molecules (g_i^t is greater than g_i^p, which is characteristic of distorted copper complexes). These g-factors made it possible to interpret subsequently the EPR spectra of the tested complexes in different phase states. In particular, it has been established for compounds **1**–**3** as well as other homologues of this series[105] that the isotropic melt actually consists of planar complexes giving rise to only one line in the EPR spectrum. Two independent lines with g-factors close to the values found for the planar and tetrahedral molecules in a single crystal of compound **1** are present in the spectrum of the mesophase (Fig. 12). It is postulated that the viscous mesophase proper is in fact formed by planar complexes, while the tetrahedral complexes are present in it as isotropic 'impurity' drops of low viscosity,[105] i.e. these molecules are separated in space.

The conformational changes in the chelate unit (*trans*-square planar → tetrahedral coordination), arising in some of the molecules during the liquid → smectic mesophase phase transition, suggest that the planar molecules are favoured by energy factors compared with the tetrahedral molecules. The corresponding calculations[89] based on the real molecular structures of compound **1** show that the conformational energy of the planar molecules is indeed smaller by ~5 kcal mol^{-1} than that of the tetrahedral molecules.

We believe that there is no doubt about the fact that two types of coordination of the metal atoms occur for copper complexes in the smectic mesophase, i.e. both planar and tetrahedral molecules are present in the mesophase. However, the specific structure of such a mesophase requires further refinement, because the claim[105] that the planar and tetrahedral complexes are separated in space is not unquestioned. Such separation actually implies the separation of the mesophase into layers, as a result of conformational transformations due to the different coordinations of the copper atoms. However, one should bear in mind that the tetrahedral complexes are nevertheless fairly anisometric, although to a lesser extent than the planar complexes, because the rotations of the ligands (~20° in compound **1** and ~10° in compounds **2** and **3**) are not so pronounced as in the classical tetrahedral complex **4** (~100°). It therefore appears doubtful that the planar molecules displace the tetrahedral molecules from their matrix, which would result in the latter being grouped together to form nonmesogenic 'impurity' drops.

The available information about the crystal packing in mesogenic substances is very useful, since certain features of the disposition of the molecules, i.e. different types of molecular associated species which are retained to some extent in the liquid-crystal state, are inherent in the mesogenic crystal. This was first pointed out by Bernal and Crowfoot[106] as early as 1933. It is essential to note that molecular packing is analysed not only with geometrical criteria (the presence or absence of layer motifs, parallel arrangement of molecules) but also energetic criteria[107] involving the analysis of the energy of molecular pair interactions. Here use is made of the concept of the structural subclass describing the relative orientation and symmetry of the molecular associated species most strongly bound by nonvalence interactions. The search for such associated species is based on the calculation of the intermolecular interaction energy by the method of atom–atom potentials. This procedure was first applied to liquid crystals by Polishchuk et al.[108] The advantage of this method, like that of conformational calculations, also based on the atom–atom approximation, consists in the fact that it operates with the structures of specific molecules and not with the approximation to the latter in the form of structureless formations (rods, discs, etc.).

A layered disposition of molecules is characteristic of the crystalline complexes **1**–**3** (Fig. 9). For compound **1**, this has been confirmed by the IMIE calculation, according to which the intralayer energy exceeds the interlayer energy by a factor of ~3.5.[8] We may note that the crystals of compounds **1**–**3** are unique objects as regards both structure (they consist of different conformers) and magnetic properties, because the magnetic interaction between the molecules within the limits of the layer is much stronger than between the layers, i.e. these objects constitute dimeric magnetic systems (see, for example, Bichkantaev et al.[104]). This is associated with the fact that the closest distance between the copper atoms in the layer is 6.5 and 5.5 Å whilst that between the layers is 21.8 and 24.7 Å for compounds **1** and **2** respectively (in the crystal of compound **3**, these distances are close to those in that of compound **2**). The data indicated above have led to the conclusion[8,89,90] that the explicit layered character of the molecular packing in compounds **1**–**3** actually predetermines the smectic mesomorphism of the above compounds.

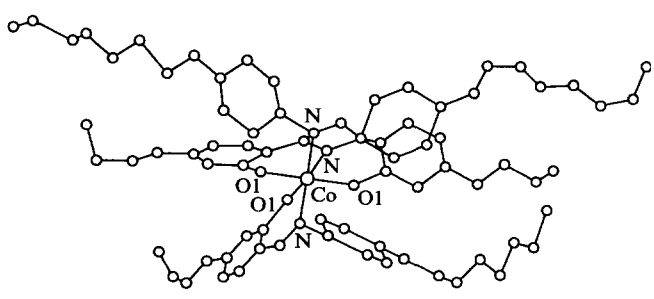


Figure 11. Molecular structure of an octahedral cobalt complex.[91]

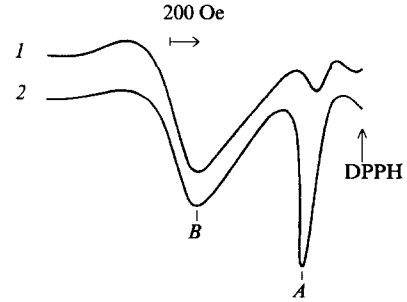


Figure 12. EPR spectrum of the mesophase of a copper complex[88] (R^1 = OC_7H_{15}; R^2 = OC_8H_{17}). External magnetic field: (*1*) parallel to the director; (*2*) perpendicular to the director; (*A*) perpendicular component of the spectrum of planar molecules (g = 2.047); (*B*) isotropic spectrum of tetrahedrally distorted complexes (g = 2.113). DPPH = diphenylpicrylhydrazyl.

Low-angle X-ray studies have shown that the thicknesses of the SmA layers in compounds **1** and **2** (d_1 = 23.6 Å, d_2 = 26.0 Å) agree with the lengths of the ligands in the corresponding complexes. Comparison of these quantities with the overall length of the molecules (30 Å in compound **1** and 26 Å in compound **2**) made it possible to put forward[109] the following models of the structures of these phases. In the case of compound **2** and also of its isostructural homologue **3** (d_3 = 26.1 Å),[90] in which the length of the molecular complexes is approximately equal to the length of their ligands, the structure of the SmA phase is usual in the sense that the thickness of the layers is specified by the overall length of the metal complexes. This is associated with the fact that in the complexes, having a transoid form, the geometrical parameters of the substituents R^1 and R^2 (Table 2) are approximately the same. On the other hand, owing to the different nature of R^1 and R^2, the overall length of the transoid complex **1** exceeds the dimensions of its ligands by a factor of approximately 1.3. Therefore the most reliable model of the layered structure of the mesophase of compound **1** is believed[109] to be that based on the crystal packing of the projection–hollow type. Fig. 9 illustrates schematically the molecular packing in the mesophase, showing the mutual migration of molecules from one layer to the other. We may note that the closest interlayer distances in the crystals of compounds **1** ($a/2$ = 21.8 Å) and **2** (c = 24.7 Å) are similar to the thickness of the layers in the mesophases (23.6 and 26.0 Å). A similar picture is observed in the smectic mesophases of the homologues with $R^1 = OC_7H_{15}$ or $OC_{12}H_{25}$ and $R^2 = C_4H_9$. Low-angle X-ray studies[110] indicate the mutual interlayer penetration of the fused alkyl 'tails' and the possible formation of pairs of copper atoms within the layers.

In order to confirm the importance of the *trans*-square planar coordination of the metal atom for the establishment of liquid-crystal properties in complexes of Schiff bases, structural and spectroscopic studies have been carried out[92] on the palladium complex **6**. It is of interest to compare the coordinations of the metal atoms and the mesomorphic properties of the palladium and copper complexes.

The replacement of copper in compound **1** by palladium does not entail a significant change in the structure of the planar molecules.[92] However, in contrast to the crystals of compounds **1**–**3**, in which both planar and tetrahedral molecules are present, the crystal structure of compound **6** is made up of only planar molecular complexes located at the centres of symmetry. The *trans*-square planar coordination of the palladium atom then remains unchanged in all phase states. This is indicated by the presence of the absorption band with λ_{max} = 402 nm in the electronic spectra of both crystalline modifications of the solution and the vitrified mesophase.[92] A similar absorption band has been attributed[111] to the square planar coordination of the palladium atom in complexes of Schiff bases.

The layered disposition of the molecules in complex **6** (Fig. 13) has been confirmed by IMIE calculations.[92] It has been noted that the presence of only planar molecules in compound **6** alters the intermolecular interaction compared with compound **1**. It is believed that the planar molecules, arranged one on top of another, interact more strongly than only tetrahedral or planar and tetrahedral molecules. This is due to the greater number of van der Waals contacts between the planar molecules, which increases their intermolecular interaction energy. The energies of the maximum pair interactions of the molecules in the layers of compounds **6** (−13.5 kcal mol^{-1}) and **1** (−11.0 kcal mol^{-1}) may be quoted to confirm this. Under these conditions, the layers in compound **6** are energetically more distinct ($U_{layer}/U_{interlayer} \simeq 5$ for compound **6** and 3.5 for compound **1**), which naturally predetermines the formation of a layered mesophase. According to Polishchuk et al.,[92] the above factors influence appreciably the range of existence of the smectic mesophase and its thermal stability, which are appreciably greater for compound **6** than for compound **1** (Table 2).

Despite the inclination of the long axes of the molecules of compound **6** relative to the layer boundary, the layered packing is similar in crystals of compounds **1** and **6**; in both cases, the arrangement of the molecules is of the projection–hollow type. Evidently, in the formation of the SmA phase the inclination of the molecules of compound **6** changes, but the characteristic features of close packing remain. This is indicated by the equal thicknesses of the smectic layers: d_6 = 23.7 Å and d_1 = 23.6 Å. Thus, in both cases the periodicity of the smectic layers is determined not by the overall length of the complexes but by the sizes of their ligands, which corresponds to distance of 22.64 Å in the crystal of compound **6** (Fig. 13).

The *trans*-square planar coordination of the metal atom has been observed also in the palladium complex **7**, having the same substituents as compound **3** (Table 2). However, in contrast to the crystal of compound **3**, in compound **7** there are only planar molecules, forming layers and evidently, as for complexes **1** and **6**, such coordination leads to higher phase transition temperatures in compound **7** than in compound **3**.

The absence of mesomorphism in the nickel complex **8** proved unexpected.[94] This complex has the same structural characteristics as the palladium complex **6** because these compounds are isostructural. It has been established that the crystals of compound **8** fuse at two temperatures (138° and 155 °C) but they do not form a mesophase, which is indicated by the absence of textures characteristic of liquid crystals in observations under a polarisation microscope. It has been noted[94] that, after the first fusion (138 °C), a dark green isotropic amorphous phase is formed, the outward form of which changes little in the second phase transition (155 °C). It is remarkable that, on repeated heating (after 24 h) of the cooled melt of compound **8**, the phase transition occurs at 348 °C and is accompanied by the decomposition of the specimen.

The authors[94] see the reason for such behaviour in the change of the coordination of the nickel atom during the fusion of the

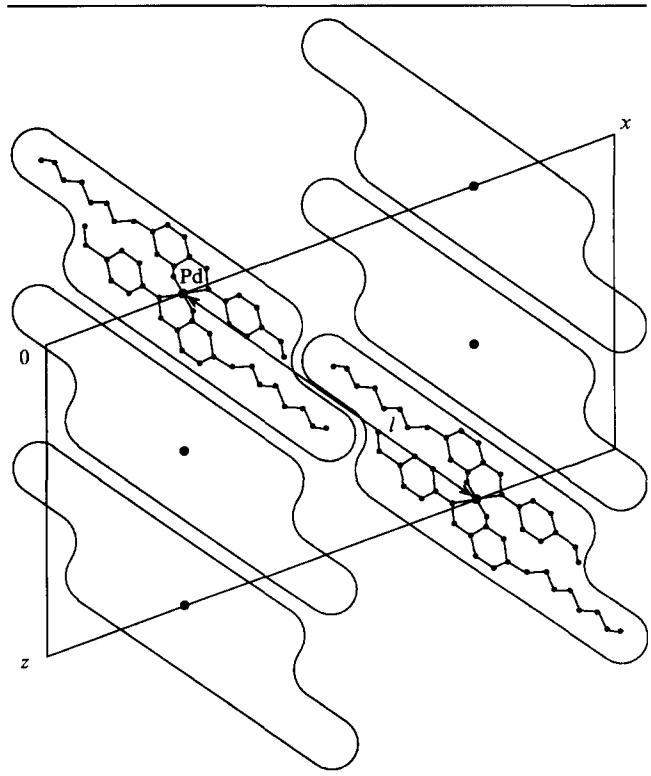


Figure 13. Molecular packing in a palladium complex. The overall form of the molecules arranged in accordance with the projection–hollow principle is indicated; l = distance between the molecules in neighbouring layers in the direction of long axes.

substance. Nickel complexes with a planar geometry of the coordination unit are diamagnetic, while those with a nonplanar coordination are paramagnetic.[112-114] The crystals of compound **8**, with a square planar coordination of the nickel, are indeed diamagnetic, which is indicated by the absence of an EPR signal in the powder of this compound at −196 °C. However, after heating to 140 °C and subsequent cooling of the melt to −196 °C, two broad lines appear in the EPR spectrum with effective *g*-factors of ~7 and ~3, indicating the transition of the test substance to the paramagnetic state. A similar situation arises[94] on fusion of the initial specimen of complex **8** to 160 °C.

Unfortunately, owing to the short spin relaxation times of the nickel compounds, their EPR signal can be recorded only at temperatures close to that of liquid nitrogen. The configurational transitions of the molecules involving a change in the coordination of nickel cannot therefore be observed by the EPR method during the heating of the specimen and directly in the melt. Studies have therefore been made[94] on the electronic spectra of the diamagnetic complex **8**, which showed that in solution in chloroform the spectrum exhibits absorption bands with maxima at 354 and 610 nm. On the other hand, an additional maximum appears in the region of 1005 nm in the spectrum of the melt after the first phase transition. These bands are retained also after the second phase transition with a slight change in their shape. According to Yamada and Takeuchi,[112] these data show that the diamagnetic complex **8** retains in solution its initial planar configuration of the unit, but on fusion and in the melt it most probably assumes a tetrahedral configuration. On the basis of the above facts, it is concluded[94] that the planar molecules of the initial specimen of compound **8** assume the tetrahedral configuration during fusion (there is a possibility of another nonplanar configuration — the octahedral configuration), which is an unfavourable factor for the establishment of the liquid-crystal state.

It is stated in a review[115] that an equilibrium mixture of isomers with planar and nonplanar structures exists as a rule in solutions of nickel complexes of Schiff bases and that the free energy of their interconversion is low (ΔG = 0.15–0.20 kcal mol^{-1} depending on the nature of the substituents in the ligands). One may postulate that the equilibrium in the melt of complex **8** is displaced towards the isomer with a nonplanar metal chelate unit. Finally, it has been noted[94] that yet another possible cause of the absence of mesomorphism in compound **8** may be a significant change in molecular structure, for example, polymerisation of the compound on fusion; the polymeric specimen then melts with decomposition at a high temperature (348 °C).

The square planar coordination of the copper atoms is very often built up to the tetragonal-pyramidal or octahedral configuration as a result of an additional intermolecular interaction. The influence of such coordination on the liquid-crystal properties of metal complexes of Schiff bases has been analysed.[95-98] Thus the copper atoms in the isostructural crystals of compounds **9** and **10** (Table 2) are in general positions and have the *trans*-square planar coordination. However, in contrast to compounds **1**–**3**, this coordination is built up to the square pyramidal as a result of the Cu ... O intermolecular interaction [the oxygen atom belongs to the metal chelate ring of a neighbouring molecule (the corresponding Cu ... O distances are 2.60 Å for compound **9**[95] and 2.62 Å for compound **10**[96])]. Such additional interaction leads to the formation of centrosymmetric coordination dimers (Fig. 14) in which the distance between the copper atoms is 3.44 Å in compound **9** and 3.46 Å in compound **10**, which is appreciably less than in compounds **1**–**3**.

The dimers in the crystals of compounds **9** and **10** form a layered packing and under these conditions the intermolecular interaction energy in the layer exceeds the interlayer energy by a factor of 3.5 for compound **9** and 4.4 for compound **10**. We may note that, in the calculation of the intermolecular interaction energy, an attempt was made[8,95] to take into account not only the dispersion component (the '6-exp' potential) of the nonvalence interactions but also the electrostatic component. However, this could not be done correctly because

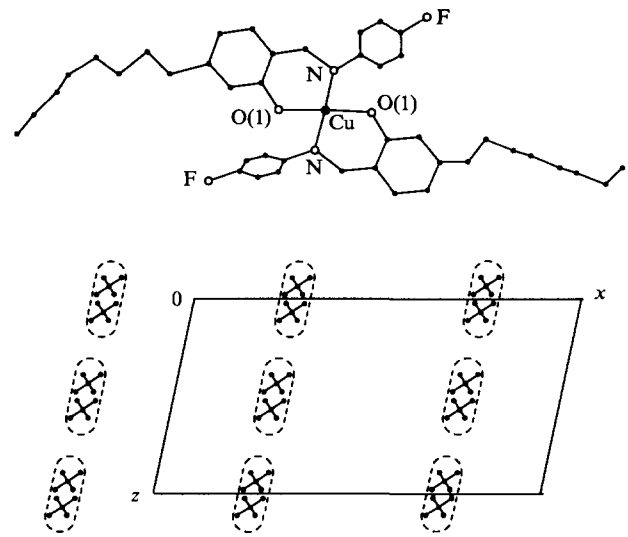


Figure 14. Molecular structure of the copper complex **9** and the packing of the central parts of the complex species in the crystal.[95] The centrosymmetric dimers are indicated by dashed lines.

it proved impossible to take into account accurately the charge distribution of the copper, nitrogen, and oxygen atoms by the semi-empirical methods employed. On the other hand, it was established that the additional intermolecular coordination enhances the interaction of the molecules in the dimers via the electrostatic component.

The observed ratio of the intermolecular interaction energies within the layers and between them for complexes **9** and **10** suggests the manifestation of smectic mesomorphism by the latter. However, an enantiotropic smectic mesophase is observed only for compound **9** (Table 2). It was assumed earlier that compound **10** does not exhibit liquid crystal properties at all (whilst the corresponding ligand does form a nematic phase[87]), but its more thorough investigation led to the observation of the monotropic SmA phase.[96] On cooling of the isotropic liquid, this phase appears just before the onset of crystallisation and exists in a very short time interval and over a very narrow temperature range. According to Polishchuk et al.,[96] the different mesomorphic behaviour of the isostructural compounds **9** and **10** can be accounted for by the different dissociation energies of the coordination dimers. This has been confirmed[95,96] by calculations of the intermolecular interaction energy: U_{dim} (**9**) = −13.9 kcal mol^{-1}; U_{dim} (**10**) = −15.2 kcal mol^{-1}. It has been noted[96] that the existence of dimers by itself need not necessarily be accompanied by the disappearance of liquid-crystal properties. Furthermore, if the dimers are characterised by an adequate anisometry, then mesomorphism is extremely likely. This is clearly seen in relation to *p*-n-alkoxybenzoic acids.[116] The O ... H–O bonds in these substances lead to the formation of dimers the anisometry of which exceeds significantly that of individual molecules. On the other hand, the dimers detected in compounds **9** and **10** have a smaller anisometry than the initial complexes of the monomeric compound. The length of such coordination dimers in fact remains the same as that of the monomer, while its transverse dimensions (or at least one of them) increase approximately by a factor of two. In this case, the dissociation energy of the dimers should play a decisive role in the formation of the mesophase. Its value should not be very great, so that the dimers do not decompose during the heating of the crystals even before the formation of the isometric liquid.

The hypothesis that the liquid-crystal properties depend on the presence or absence of coordination dimers has been confirmed by EPR studies. It has been noted[96] that he EPR spectra of compounds **9** and **10** are identical and that they are characterised by the presence of a fine structure and a forbidden

transition ($\Delta M_s = \pm 2$) (Fig. 15). When powdered compound **9** is heated, the EPR spectrum is modified at the instant of the formation of the SmA phase (130.1 °C, Table 2): the fine structure vanishes and a spectrum characteristic of monomeric copper complexes appears (Fig. 12).[105] The spectra indicate the absence of dimers over the entire range of existence of the SmA phase and also in the isotropic phase on further heating. We may note that the mesophase of compound **9** is characterised by a layer thickness of 22.4 Å, which is close to the length of an individual ligand. This finding indicates, as for the smectic phases of compounds **1** and **6**, an arrangement of the molecules of the projection–hollow type, which is characteristic also of the crystal structure itself, where the distance between the molecules in neighbouring layers is equal to half the maximum period $a/2$ = 19.91 Å.

Heating of compound **10** entails the same changes in the EPR spectrum as in the spectrum of compound **9**. However, in this case the fine structure due to the dimeric organisation of the molecules vanishes at the instant of fusion of the substance to the isotropic liquid (150.1 °C), in which only monomeric complexes are present.

Thus EPR data show that the dimers in compound **10** decompose at a higher temperature than in compound **9**, which is the reason for the monotropic smectic mesomorphism of compound **10**. In other words, the temperature range of the possible existence of the mesophase in compound **10** is, as it were, 'jumped over' on heating by virtue of the higher dissociation energy of the dimers compared with compound **9**. At the same time, the temperatures of the transition to the isotropic liquid are virtually identical for both compounds.

The negative influence of the additional intermolecular coordination on the formation of the mesophase was manifested even more evidently in the isostructural copper complexes **11** and **12** containing polar ligands. These compounds were obtained by procedures similar to those used for the compounds described by Ovchinnikov et al.[87]—by refluxing in absolute ethanol equivalent amounts of the 4-heptyloxy-*N*-(4′-cyanophenyl)- and 4-heptyloxy-*N*-(4′-nitrophenyl)-2-benzylidenehydroxyamine with copper acetate for compounds **11** and **12** respectively. In the crystal structures of compounds **11**[97] and **12**[98], the copper atoms occupy general positions and are characterised by a *trans*-square planar coordination. As in complexes **1**–**10**, the benzene rings in these compounds, condensed with chelate rings, are parallel to the planar fragments of the chelate rings, while the phenyl substituents at the nitrogen atoms have undergone significant rotation. At the same time, the presence of the polar CN and NO_2 groups in the ligands builds up the coordination of the copper atoms to the square-bipyramidal as a result of the Cu...N intermolecular interaction for compound **11** and the Cu...O interaction for compound **12**. Such additional coordination promotes the formation in these crystals of the so called infinite coordination strata, the thickness of which is determined by the transverse dimensions of the molecules (Fig. 16). The thickness of the layered associated species is determined by the length of the molecule and this constitutes the main difference between strata and layers. The presence of strata has been confirmed by calculations of the intermolecular interaction energy (without taking into account the electrostatic component), according to which the energy of the interaction of the molecules in the strata is approximately six times greater than that between them.[97] One has to assume that the additional intermolecular coordination intensifies to an even greater extent the interactions of the molecules in the strata via the electrostatic component, which is evidently responsible for the high temperatures of the conversion of compounds **11** and **12** into the isotropic state (Table 2).

According to Polishchuk and coworkers,[97,98] the formation of the mesophase by compounds **11** and **12** is accompanied by the disruption of the infinite coordination strata and the disappearance of the additional intermolecular coordination, which is similar to the decomposition of the dimers in compounds **9** and **10**. Indeed, when the crystals are heated, an isotropic liquid consisting of individual molecules with the anisometry of the molecular complexes characteristic of the square planar coordination of copper is formed. During the heating of the isotropic melt of compound **11**, the planar molecules form a nematic mesophase in a narrow temperature range near 10 °C, which vanishes following the onset of the restoration of the additional coordination, i.e. on crystallisation. In the case of compound **12**, the intermolecular coordination is evidently restored faster on cooling of the isotropic melt, as a result of which the crystallisation of the specimen sets in immediately. The absence of the liquid-crystal state for compound **12** (in contrast to the monotropic mesomorphism of complex **11**) is associated, according to the authors,[98] with the stronger additional interaction in the latter case. This is indicated indirectly by the intermolecular coordination distances. When account is taken of the van der Waals radii of the oxygen atoms (1.29 Å)[117] and nitrogen atoms (1.50 Å),[118] they are smaller for the complexes with the NO_2 group (Cu...O = 2.88, 2.91 Å[98]; Cu...N = 3.10, 3.47 Å[97]).

Thus analysis of the above studies[96–98] indicates the negative influence of the additional intermolecular coordination in

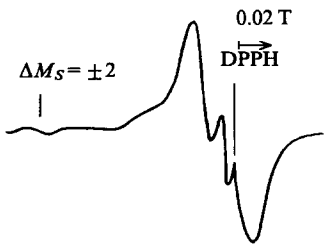


Figure 15. EPR spectrum of the powdered crystalline copper complex **10** at room temperature.[96] The presence of the fine structure and of the forbidden transition $\Delta M_S = \pm 2$ is due to the presence of coordination dimers.

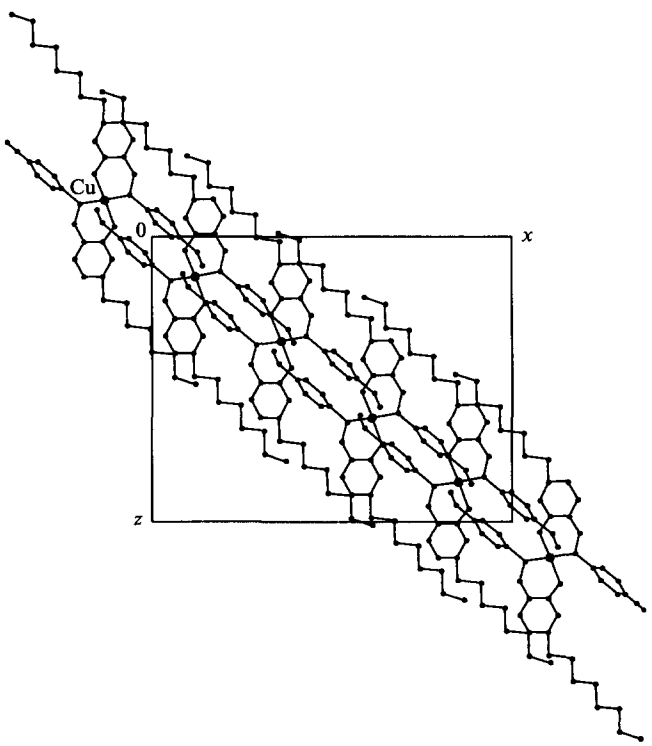


Figure 16. Molecular packing in strata in the crystalline copper complex **11**. Only the central stratum is shown. The thickness of the strata is determined by the transverse dimensions of the molecules.

compounds **10**–**12** and the establishment of the liquid-crystal state, which is expressed either by the presence of only monotropic mesomorphism or by the absence of any kind of liquid-crystal properties. This claim is supported by the finding that individual ligands of the above complexes do exhibit mesomorphism.[87,119]

Among all the complexes of Schiff bases considered here, compound **13** exhibits the maximum molecular anisometry. In the crystal, its molecules are located[99] at the centres of symmetry and are characterised by a *trans*-square planar coordination of the copper atoms. The increase in the length of the mesogenic molecules intensifies the lateral interaction between them, which ensures the appearance of the smectic mesophase. We may note that the copper complexes tend in the main to exhibit smectic mesomorphism (Table 2), while their ligands form a nematic phase. This has been explained in a study,[96] where it was stated that transoid metal complexes are longer by a factor of 1.3–1.4 than their ligands. Furthermore, the lateral interaction of the metal complexes intensifies as a result of the greater number of benzene rings in the central part of the molecules. Taking these facts into account, one would expect the formation of the smectic phase of compound **13**, particularly since its ligands exhibit these properties (smectic phase A at 43–148 °C and a nematic phase at 148–164 °C). However, this compound forms only a nematic mesophase (Table 2), which is caused, according to Polishchuk et al.,[99] by the characteristics of the molecular packing, especially by the presence of chain associated species. Calculations of the intermolecular interaction energy showed that energetically segregated chains of molecules are formed in the crystal in the direction along the x axis and that the energy of the strongest interaction in them is -16.4 kcal mol^{-1}. The assembly of such chains forms strata parallel to the crystallographic xy plane. It is emphasised[99] that the energetic preference for the formation of strata (the interaction of the molecules within the strata is more than 8 times more intense than the interaction between the strata) is in the main associated with an intrachain interaction, which contributes about 55% to the total energy of the interaction of molecules in the strata. It has also been suggested[99] that this interaction intensifies still more via the electrostatic component, because the coordination of the copper atoms in the chains is close to the square-bipyramidal owing to the additional Cu ... O (3.94 Å) intermolecular interaction.

According to the authors,[99] the intense interaction between the molecules in the chain inhibits smectic isomorphism just as the dimers or coordination strata prevent the formation of the mesophase in complexes **10**–**12** examined above. However, such interactions were apparently insufficient to inhibit also the nematic phase. When complex **13** is heated, the formation of the nematic phase entails the rupture of the chain associated species without affecting at the same time the parallel arrangement of the long molecular axes characteristic of this mesophase. On cooling the melt of compound **13**, such associated species are not restored immediately owing to thermal motion and the temperature range of the existence of the nematic phase is appreciably extended (ΔT = 75 °C) compared with the analogous region arising on heating (ΔT = 5 °C, Table 2). In other words, the chain associated species in compound **13** prevent the appearance of the smectic mesophase both on heating and on cooling and, furthermore, cause significant narrowing of the temperature range corresponding to the existence of the nematic mesophase during the heating of the specimen.

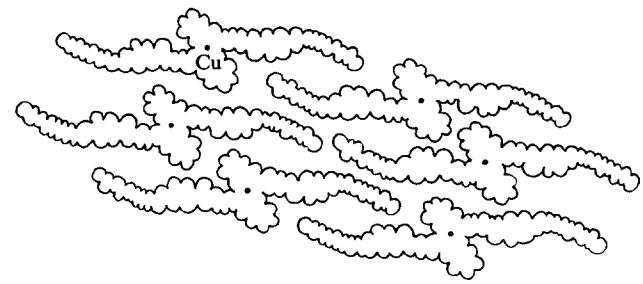
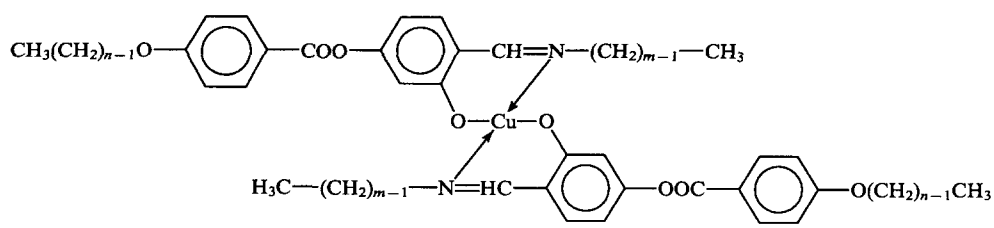


Figure 17. Model of the molecular packing in the nematic phase of the copper complex **13**.

Together with the description of the dependence of the liquid-crystal properties on the additional coordination of the metal atom, much attention has been devoted by Polishchuk et al.[97–99] to the analysis of the geometrical characteristics of the molecular associated species. In particular, it is emphasised that[97] the formation of molecular strata is unfavourable for the manifestation of smectic mesomorphism. As mentioned above, the thickness of the strata in compounds **11** and **13** is determined by the transverse dimensions of the molecules, whereas in the classical smectogenic crystals the thickness of the layer is comparable to the longitudinal dimensions, i.e. the length of the molecules. Furthermore, in smectogenic crystals the interlayer interaction energy is largely determined by the 'end-face' interactions between the alkyl chains of the molecules in neighbouring layers (see, for example, Fig. 9). On heating such crystals, the 'fusion' of the chains, characterised in the crystalline state by high thermal parameters,[8] begins at lower temperatures compared with the central rigid fragments. As a result of such partial fusion, there is a possibility of almost free sliding of the smectic layers relative to one another. Such nature of the fusion with the initial increase in the mobility of the terminal alkyl substituents has been demonstrated by NMR[120] and EPR methods with the aid of spin labels in the aromatic and aliphatic parts of the molecules.[121] On the other hand, in crystals with a stratified structure the sliding of the strata relative to one another is difficult, because not only the atoms of the alkoxy-chain but also those of the central rigid fragments, characterised by significantly weaker thermal vibrations, participate in the contacts between the strata.

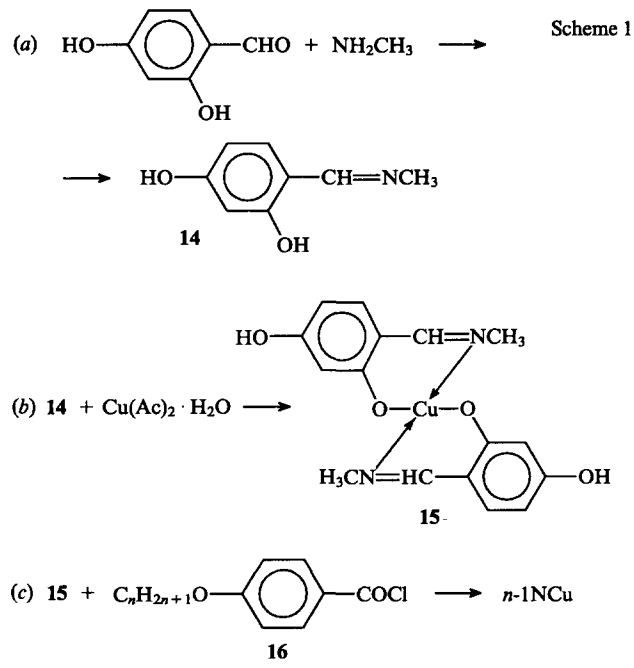
As in the smectic mesophases of compounds **1**, **6**, and **9**, the periodicity of the nematic phase in compound **13** (l_{13} = 34.0 Å) is determined by the length of the ligands (~37 Å). This leads to molecular packing of the projection–hollow type. However, in contrast to the smectic mesophases, in the nematic mesophase of compound **13** the intermolecular end-face contacts are varied. In particular, contacts between the carbon atoms of the condensed benzene rings, contacts between the same rings and the alkoxy-chains, and finally contacts between the chains themselves occur in this case (Fig. 17).

A series of studies devoted to new copper complexes with similar ligands have been published recently. Thus the synthesis and characteristics of the phase transitions in the metal complexes *n*-*m*NCu with the structural formula have been described by Caruso and coworkers.[122,123] The compounds with m = 1 and n = 6–14 (*n*-1NCu) were synthesised as follows.[122]

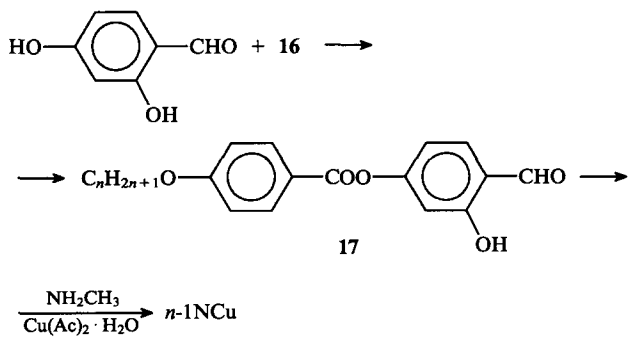


Complex *n*-*m*NCu

Scheme 1



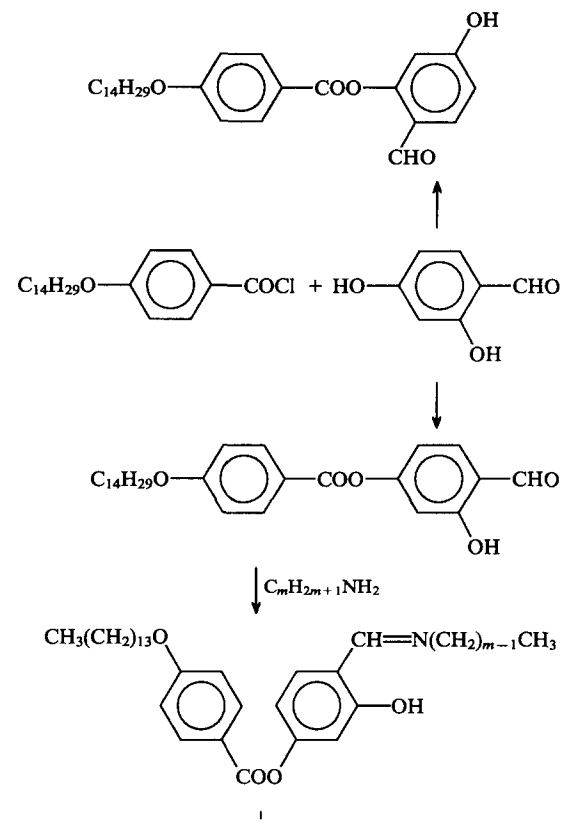
Scheme 2



The compounds with n = 7, 10, and 14 were obtained in accordance with Scheme 1, whilst all the others were obtained in accordance with Scheme 2. All the compounds with n = 6–14 can be obtained in accordance with one of the two schemes, but the authors[122] quote two schemes in order to illustrate different versions of the synthesis. All the compounds are enantiotropic mesogenic substances. For n = 6–9, only the nematic phase is observed, but, with increase in n from 10 to 13, both nematic and smectic phases appear. Finally, for n = 14 only the SmC phase exists. It is noted that in the above homologues there is no even-odd effect in the temperatures of the transition to the isotropic state and the enthalpies per unit mass are appreciably smaller compared with the usual organic mesogenic substances containing symmetrical alkoxy-chains of the corresponding length. It is of interest that in all the smectogenic homologues with n = 10–14 solid-crystal transitions were observed. Thus, in the compounds 13-1NCu and 14-1NCu, these transitions have been confirmed by X-ray powder diffraction studies. It is emphasised here that the layered character of the packing in the crystalline modifications, which are precursors of the mesophase, is correlated with the smectic mesomorphism.

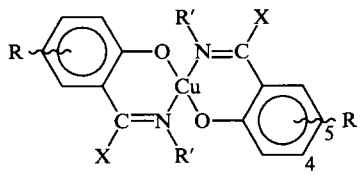
Data have been published[123] on the liquid-crystal properties in the homologous series of copper complexes containing alkylamino-groups with m = 2–15. The need to elucidate the dependence of the mesogenic properties on the length of the alkylamino-groups in the complex 14-1NCu, which itself forms only the SmC phase, led to the synthesis of these compounds.

The compounds with m = 2–15 (14-mNCu) were synthesised in accordance with the following scheme.



In the series of metal complexes 14-mNCu obtained, only the homologue with m = 2 has no liquid-crystal properties. This has been explained[123] by the impairment of the conditions for the effective packing of molecules along their short axis, which is induced by changes in molecular structure compared with the smectogenic homologue with m = 1. Evidently the conformation of the ethyl groups at the nitrogen atoms weakens the lateral interaction between the molecules. The presence of only the nematic phase N is characteristic of the homologues with m = 3–9, while the presence of the mesophases N and SmC is characteristic of the homologues with m = 10–15. Low-angle X-ray studies on the compounds 14-14NCu and 14-15NCu showed[123] that the periodicities of their smectic layers, amounting to 35.3 and 36.3 Å respectively, are significantly smaller than the analogous periodicity for the compound 14-1NCu (43.3 Å).[122] These results show that, despite the identical type of the mesophases (SmC), the molecular packing within smectic layers changes appreciably. These changes are most probably associated with the inclination of the long molecular axes with respect to the boundary of the layer, which is smaller for 14-1NCu. The majority of the compounds of the 14-mNCu series undergo solid-crystal phase transitions, which are not always reproducible and which depend on the rate of heating and cooling of the specimens. It has also been noted[123] that the crystals of certain homologues, obtained from solution and the melt, have different structures and melt at different temperatures. We emphasise that the solid-crystal polymorphism, characteristic of liquid-crystal compounds, is as a rule associated with conformational changes in the mobile groups, in particular in aliphatic chains. Cholesteryl benzoate, for which six modifications have been found[124] and the single crystals of three of them have been investigated by X-ray diffraction,[125] may serve as a typical example.

A more detailed analysis of the dependence of the liquid-crystal properties on the structural characteristics of the molecule has been carried out[126] for complexes of the type

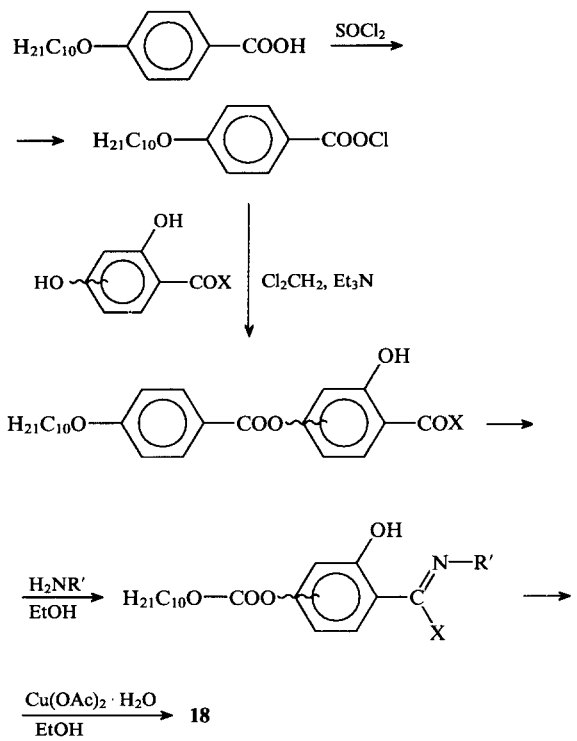


18

R = O—C(=O)—C$_6$H$_4$—OC$_{10}$H$_{21}$ (in the 4- or 5-positions);

R′ = CH_3, *p*-$C_{10}H_{21}$, $C_6H_4OC_{10}H_{21}$; X = H, CH_3.

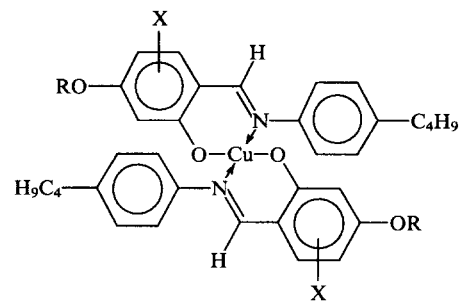
They were synthesised as follows:



Mesomorphism is characteristic of complexes of this kind (Table 3). Its manifestation is legitimately attributed to the molecular shape, which depends significantly on the disposition of the substituents (Figs 18 and 19). Table 3 shows that the complexes with X = H and R in the 4-position possess liquid-crystal properties and for R′ = $C_6H_4-OC_{10}H_{21}$ two smectic phases, SmC and SmI, have been found. The latter has been identified as SmG.[10,127] The authors[126] mention particularly the different types of mesophases for *N*-alkylimines. For complexes with R′ = CH_3, there exist both SmC and N mesophases, while for R′ = *p*-$C_{10}H_{21}$ there is only an N mesophase. The reason for this is that the long and conformationally mobile decyl groups, parallel to the main molecular axis (Fig. 18), interfere with the establishment of the packing equivalent to the smectic mesophase. They can serve as a shield preventing interaction between the rigid aromatic rings of the molecules. On the other hand, the comparatively small size of the methyl groups makes it possible to increase the effectiveness of this interaction, which results in the appearance of the more ordered mesophase SmC and the thermal stability increases by 90 °C (Table 3). We may note that the interaction between the central parts of the mesogenic molecules should be optimum for the formation of the smectic mesophase. When the layers are insufficiently distinct in energetic terms, they do not persist during fusion. As a consequence of the unduly intense interaction (the presence of coordination dimers, chains, networks, etc.), the melting point increases and the temperature range corresponding to the smectic mesophase can be 'jumped over' under these conditions and in many cases there may be no mesomorphism at all. We believe that the second factor is the reason why only the nematic mesophase arises[128] at 223 °C in one of the representatives of the 2,4-hydroxy-derivatives of the complexes considered (X = H, R′ = $C_6H_4-C_5H_{11}$, n = 4). It has been established that the copper atom is involved in a distorted square-pyramidal coordination with an angle of twist of 22° between the two coordination planes formed by copper, oxygen, and nitrogen atoms and is also involved in an additional interaction (Cu ... O = 3.04 Å) with the ester carbonyl group of a neighbouring molecule.

The overall structure of 2,5-dihydroxy-derivatives of the complexes differs appreciably from that of the 2,4-disubstituted derivatives. Such complexes can be represented schematically by a long rod with side substituents R′, which prevent a parallel ordered arrangement of the molecules in the mesophase (Fig. 19). This is why only the *N*-methylamine complex (R′ = CH_3, X = H) forms a mesophase (Table 3). For longer substituents R′, such molecules undergo a decrease in their anisometry, as happens on replacement of a copper atom in complex **18** (see above) by a cobalt atom. The absence of liquid-crystal properties in the complexes with X = CH_3 is due to the steric effects of the methyl groups, which distort the square planar coordination of copper in the direction of tetrahedral coordination.[126]

The mesomorphism of copper complexes with halide substituents in the 3- and 5-positions has been examined.[129] It was noted that the overall anisometry of the molecular complexes and the transition temperatures vary little as a



R = R′O—C$_6$H$_4$—C(=O)—CH$_3$

R′ = C_nH_{2n+1}, n = 4, 8, 12, 16;

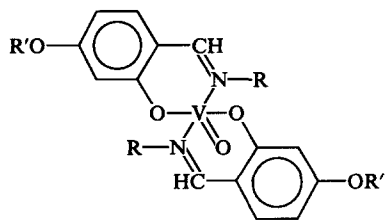
X = Cl, Br (in the 3- or 5-positions).

function of the positions of the halogen atoms.

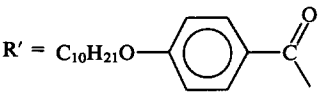
Complexes of other metals [VO[130,131] and iron(III)[132]] with Schiff bases have been investigated in lesser detail hitherto. In particular, the VO complexes (R = Me, C_5H_{11}, $C_{10}H_{21}$, etc.) described[131] have a square-pyramidal coordination and form both nematic and smectic (SmC) paramagnetic mesophases.

The synthesis of these compounds has been undertaken in order to obtain a biaxial nematic mesophase, but this attempt proved unsuccessful. Nevertheless, it has been observed that these compounds have a series of interesting properties.

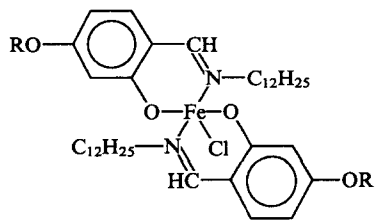
Thus the low viscosity of the nematic mesophase permits a ready orientation of the molecule by a magnetic field, such orientation remaining unchanged also in the solid-crystal state (in the presence of a magnetic field), which indicates the similarity of the molecular packing in these states.



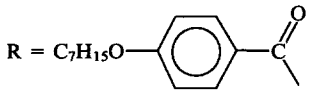
R = Me, *p*-C_5H_{11}, *p*-$C_{10}H_{21}$, C_6H_4–OMe, C_6H_4–OEt, $C_6H_4-OC_5H_{11}$, $C_6H_4-OC_{10}H_{21}$;



The paramagnetic mesogenic iron(III) complex **19** (g_1 = 2.096, g_2 = 4.30) forms a smectic phase (85–151 °C) and is probably characterised by a square-pyramidal coordination of the metal atom.[132]

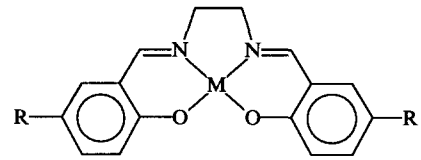


19



Another type of coordination of the metal atom to salicylideneanime ligands occurs in di(5-substituted) salicylideneethylenediamine complexes of nickel(II) and copper(II) described by Paschke et al.[133]

The formation of type SmA smectic phase is characteristic of these complexes. It has been possible to carry out an X-ray diffraction study on a single crystal of the nickel(II) hydrate complex with R = OC_6H_{13}. Layered associated molecular formations, characteristic of crystalline precursors of smectic mesophases, were not detected in the crystal. The molecules in the crystal form centrosymmetric dimers, which are arranged in stacks with a superimposed 'herringbone' pattern. However, on the basis of these results, one cannot conclude that there is no similarity between the structures of the solid- and liquid-crystal phases, since the hydrate of the complex was investigated by X-ray diffraction and the presence of water molecules might have exerted a significant influence on its packing in the crystal.

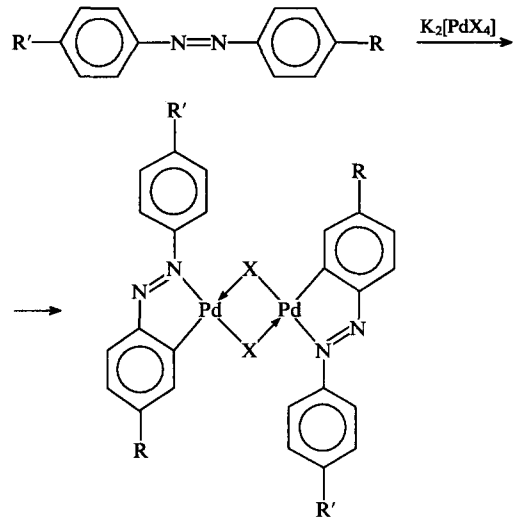


R = OC_nH_{2n+1}, C_nH_{2n+1}, n = 5–10.

7. Mesogenic palladium complexes

Mesogenic palladium complexes are usually segregated in a separate group, since mesogenic compounds in which the metal atom forms part of a cyclic fragment have been found only among them. A distinctive feature is that the palladium atom in the complexes forms a Pd–C(sp^2) σ-bond with a carbon atom of the benzene ring, i.e. such compounds can be regarded as organometallic.

The synthesis of liquid crystals of cyclopalladate complexes has been described for the first time by Chedini et al.[134]



X = Cl; R = OEt or Et; R′ = $COOC_4H_9$, $COOC_5H_{11}$, $COOC_6H_{13}$, or $COO(CH_2)_8CH=CH_2$.

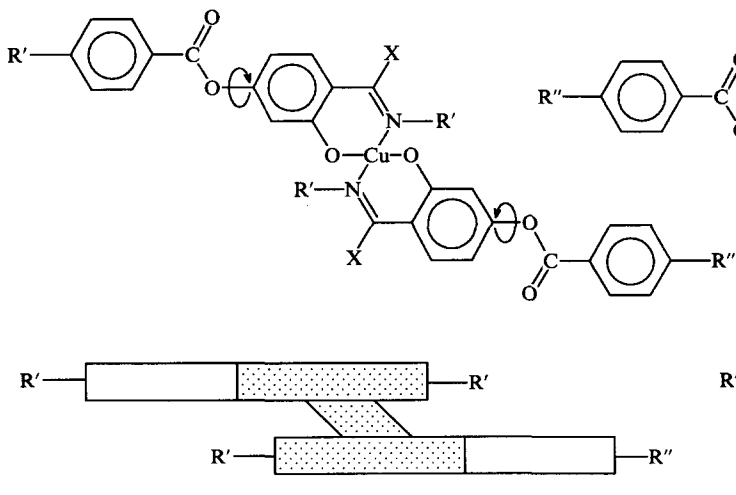


Figure 18. Structural formula and representation of the overall form of the molecule of a 2,4-disubstituted copper complex[126] (R″ = $OC_{10}H_{21}$). The rigid central fragment of the molecule is shown dotted.

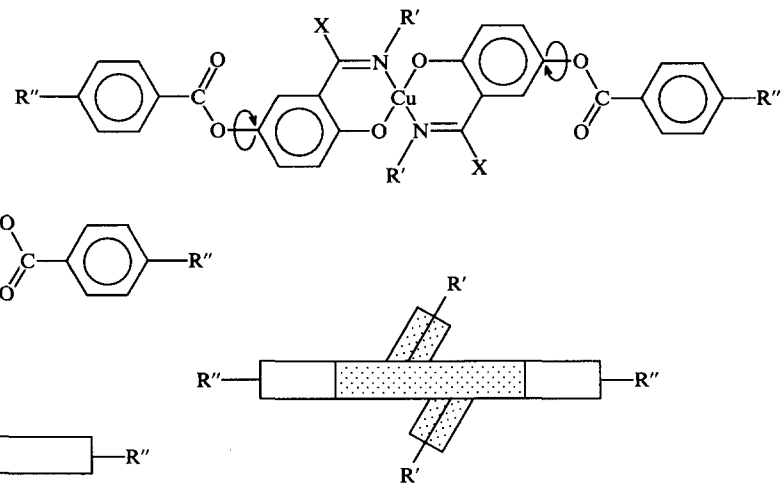


Figure 19. Structural formula and representation of the overall form of the molecule of a 2,5-disubstituted copper complex[126] (R″ = $OC_{10}H_{21}$).

Table 3. Characteristics of the phase transitions in complexes **6**.

X	Position of R	R′	Phase transition temperatures/ °C
H	4	$C_6H_4-OC_{10}H_{21}$	C $\xrightarrow{120.6}$ SmI $\xrightarrow{163.6}$ SmC $\xrightarrow{247.9}$ N $\xrightarrow{248.5}$ I
H	5	$C_6H_4-OC_{10}H_{21}$	$C_1 \xrightarrow{59.2} C_2 \xrightarrow{119.0} C_3 \xrightarrow{119.2} I$
H	4	p-$C_{10}H_{21}$	C $\xrightarrow{115.7}$ N $\xrightarrow{134.0}$ I
H	5	p-$C_{10}H_{21}$	C $\xrightarrow{103.9}$ I
H	4	CH_3	C $\xrightarrow{173.9}$ SmC $\xrightarrow{178.2}$ N $\xrightarrow{224.0}$ I
H	5	CH_3	C $\xrightarrow{187.4}$ SmC $\xrightarrow{237.5}$ N $\xrightarrow{265.7}$ I
CH_3	4	$C_6H_4-OC_{10}H_{21}$	$C_1 \xrightarrow{106.5} C_2 \xrightarrow{184.3} C_3 \xrightarrow{201.0} C_4 \xrightarrow{228.0} I$
CH_3	5	$C_6H_4-OC_{10}H_{21}$	C $\xrightarrow{190.0}$ I
CH_3	4	p-$C_{10}H_{21}$	C $\xrightarrow{142.3}$ I
CH_3	5	p-$C_{10}H_{21}$	C $\xrightarrow{115.6}$ I

These compounds form a nematic phase at a fairly high temperature (~200 °C), which rises in the sequence I > Br > Cl (R = OEt, R′ = C_6H_{13}).[135,136]

The results of optical, calorimetric, and IR spectroscopic studies on certain mesogenic azobenzene compounds and their metallocyclic palladium complexes with R = CH_3 or C_2H_5, R′ = C_nH_{2n+1}, and n = 1, 2, 7, and 12 have been compared.[137] The mesophase consists of a 1 : 1 mixture of complexes in which R and R′ change places. These investigations enabled the authors to observe an optically biaxial nematic mesophase in the palladium complexes. The presence of the biaxial nematic phase in these complexes was detected by observing the conoscopic pattern, which was found to contain split monoaxial crosses.[137] This effect (the splitting of the crosses) intensifies still more on imposition of a magnetic field. It has also been noted that the changes in the enthalpies and entropies of the N → I phase transitions are appreciably smaller for the complexes than for the ligands. According to Galerne,[138] this is associated with the molecular biaxial arrangement. It is emphasised[137] that the order parameter P_2 for the complexes is systematically lower than the analogous value for the corresponding ligands (Fig. 20).

The authors discussed this change in P_2 within the framework of the theory of Luckhurst et al.[139] for biaxial molecules and concluded that the incomplete agreement with this theory can be accounted for either by the inaccurate expression for the pseudopotential or by the fact that the biaxial ordering occurs only at a local level, where P_2 is merely one of the components of the order parameter tensor. We emphasise that in the complexes described the biaxial nature of the nematic phase is due to the molecular structure, because the length of the molecules in the complexes is identical with the length of the molecules of the monoaxial ligands, while the width is approximately twice as great.

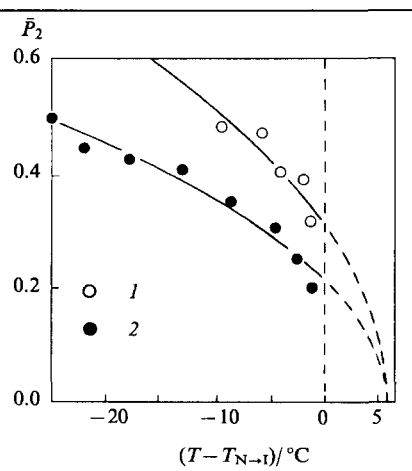
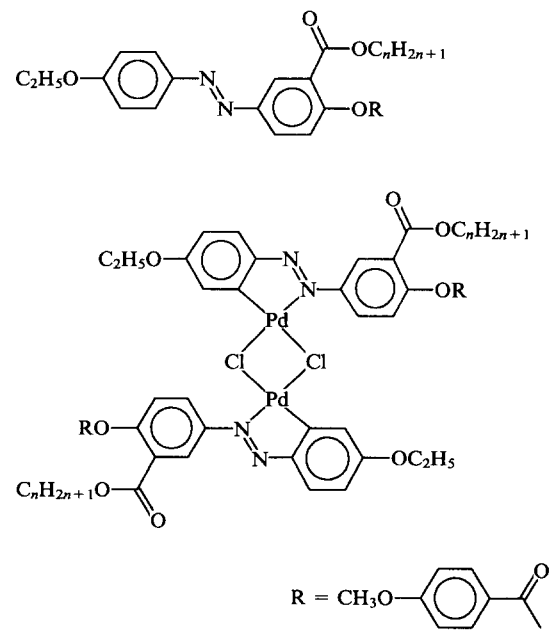


Figure 20. Temperature variation of the order parameter P_2. $T_{N\to I}$ is the temperature of the phase transition N → I; (*1*) complex; (*2*) ligand.

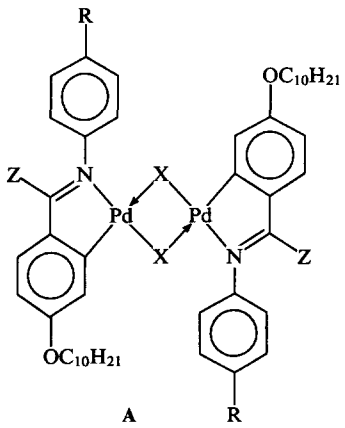
Similar complexes have been obtained from ligands containing three benzene rings and which have been described by Hoshino et al.[140] The ligand and the complex have the following form:



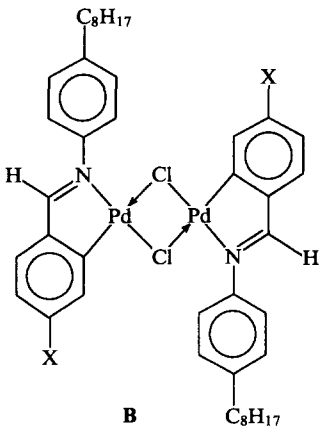
The homologous series with n = 1–10, 12, 14, 16, and 18 has been investigated. Both the ligands and the complexes proved to be nematogenic compounds, the temperature ranges corresponding to the existence the mesophases of these homologues varying in parallel. The average melting point of the complexes is higher by 87 °C and the clarification temperature is higher by 126 °C than the corresponding temperatures for the ligands. ^{1}H NMR data suggested that the most favourable conformation, at least for long-chain homologues, is that in which each substituent

$COOC_nH_{2n+1}$ occupies a position between the main phenyl-containing chains of the ligands. According to Hoshino et al.,[140] this conformation is most favourable for the formation of a nematic phase by the above compounds.

The synthesis of complexes of two types from the corresponding Schiff bases and $Pd_3(OAc)_6$ has been described.[141–144] Complexes A form mainly mesophases of the SmA type with the following bridging groups: X = Cl, Br, or SCN; the acetate-bridged complexes are in most cases nonmesogenic, which may be associated with the distortion of the planarity of the central part of the molecules. Mesomorphic behaviour is also characteristic of chloride complexes of type **B**.



A



B

In contrast to the complexes mentioned above, a complex with a different type of acetate bridge (X = $MeCO_2$), obtained from the symmetrical 4,4′-bis(alkoxybenzylidene)hydrazine $C_nH_{2n+1}OC_6H_4CH = N-N = CHC_6H_4OC_nH_{2n+1}$ (n = 7, 10, 12, 14), forms an SmC mesophase. Evidently the μ-acetate ligands distort the planarity of the central part of the molecular complexes, which made it necessary to segregate them[145] as a new type of structure referred to as 'open book' structures (Fig. 21).

Special mention should be made that, according to NMR data, an optically active complex of this series (n = 10) (Fig. 21) contains a mixture of the *trans*-λ-R,R-, *trans*-δ-R,R-, and *cis*-R,R-isomers.[146] This compound forms an enantiotropic SmC* phase and is the first organometallic ferroelectric substance. However, its electrooptical response is significantly weaker than for organic calamitic phases SmC* owing to its high viscosity, which is probably due to its large molecular volume.

8. Liquid-crystal complexes of phthalocyanines

Mesogenic phthalocyanines (Pc) constitute a new class of potential liquid-crystal one-dimensional conductors,[147–150] in which the direction with maximum conduction coincides with the direction of the columns. The columns themselves are made up of flat polar

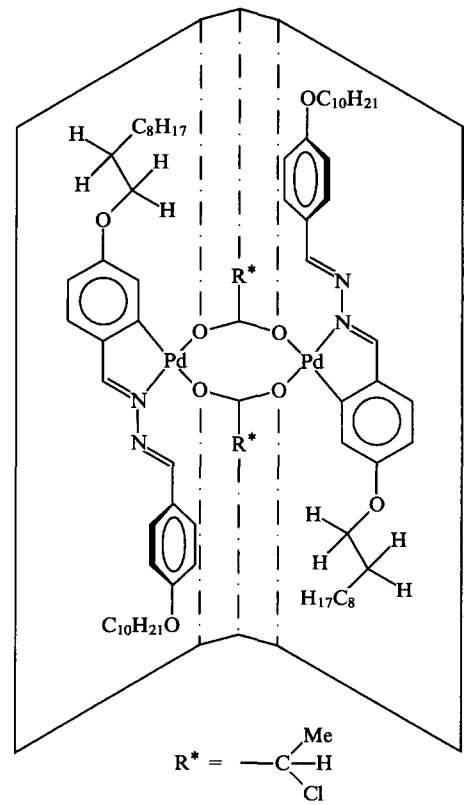
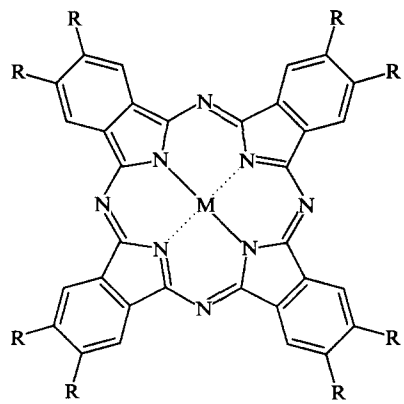


Figure 21. An optically active complex having the open book conformation.[146]

aromatic nuclei separated by neutral fused paraffin chains. It is possible to obtain phthalocyanine complexes of different metals: Fe, Co, Ni, Cu, Zn, and Pt. This allows one to vary their electronic properties. The presence of stacks with a fairly strong interaction of the molecules within them and appreciably weaker interactions of the molecules between the stacks is characteristic of such compounds in the crystalline and liquid-crystal states. Thus such interaction gives rise to anisotropy of the electronic transport properties.

The mesomorphic, structural, optical, and electrical properties of a large number of phthalocyanine compounds having the general formula



M = 2H, Cu,
R = OC_nH_{2n+1}, n = 6–12.

have been examined in detail in a review article.[151]

The copper complexes (CuPc) were synthesised by deprotonating the free ligands with sodium pentyloxide and subsequent interaction with anhydrous copper(II) chloride. Low-angle X-ray studies[151] showed that all the Pc homologues

and the corresponding copper complex CuPc form a discotic ordered hexagonal mesophase D_{ho}. According to electron-diffraction data, the molecular stacks in the crystals are then disposed along the long axes of the acicular crystals, for which ~20–25 diffraction lines are observed. The indexing of these lines showed that the crystals belong to the orthorhombic system with $Z = 4$. The calculated densities (1.1 g cm^{-3} for $n = 12$ and 1.4 g cm^{-3} for $n = 6$) of the complexes CuPc agree with the values established previously (1.6 g cm^{-3} for CuPc[152] and 1.1 g cm^{-3} for the phthalocyanine complex with R = $CH_2OC_{12}H_{25}$[148]). In all cases the (001) reflections correspond to a distance of ~4.3 Å between neighbouring molecules within each stack. This fairly large distance indicates an inclined disposition of the molecules relative to the axes of the stacks. This is also indicated indirectly by the change in the unit cell parameters a and b as a function of n (Fig. 22). On average, both parameters increase with increase in n, but van der Pol et al.[151] suggest that the more marked change in the parameter b indicates a change in the inclination of the molecules precisely relative to this direction.

The electron diffraction pattern of the mesophase in the region of low angles contains five reflections ($l/d = 1 : \sqrt{3} : \sqrt{4} : \sqrt{7} : \sqrt{9}$) corresponding to a hexagonal lattice, the broad diffuse reflection (4.6 Å) corresponding to the disordered structure of the aliphatic chains. At the same time, the X-ray diffraction patterns of all the homologues of Pc and CuPc contain an intense and sharpened reflection (3.4 Å) due to the ordered arrangement of the molecular discs within one column. Finally, the weak and broad reflection (7.0 Å) is attributed to some kind of ordering within the columns, but one cannot rule out the possibility that this is a second-order manifestation of the 3.4 Å periodicity.

The dependence of the distances D between the columns in Pc and CuPc (parameter of the planar hexagonal unit cell) on the length of the alkyl chain is almost linear (Fig. 23).

Comparison of the values of D found with the calculated diameter of the nuclei (taking into account the oxygen atoms) D_c = 16.8 Å and with the length of the extended n-alkyl chain indicates an appreciable interpenetration of the alkyl chains of neighbouring columns up to their contact with the phthalocyanine nuclei of neighbouring columns. The fact that the value D_c = 16.8 Å does not differ greatly from that established (13.9 Å) for unsubstituted phthalocyanine[153] and is close to the model estimates (17.0 Å) led the authors[151] to the conclusion that the planes of the nuclei of the phthalocyanine molecules in the mesophase are on average disposed at right angles to the axis of the column (if they were inclined, the value of D_c would be even

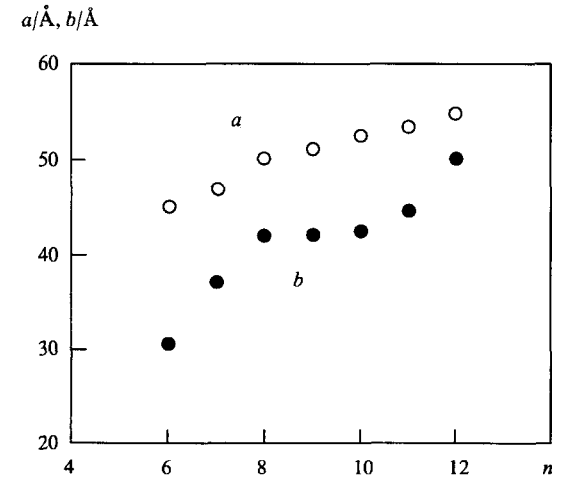


Figure 22. Dependence of the parameters a and b of the orthorhombic lattice on n in the homologous series of complexes CuPc.

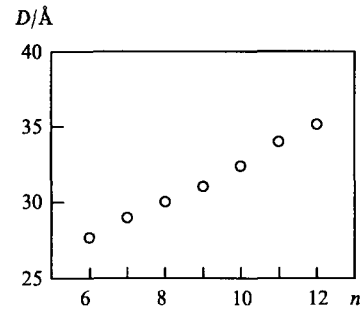


Figure 23. Variation of the distance between the columns in Pc and CuPc as a function of the length of the alkyl chain.[151]

smaller). Such stacked arrangement of the nuclei of the molecules is in fact favourable for the exciton and electron migration through the column. We may note that the inclined disposition of the molecules is frequently encountered in discotic mesophases. Thus the study of freely suspended films of triphenylene hexa-n-dodecanoate using synchroton radiation established[154] that in both phases, D_{hd} and D_{rd}, the nuclei of the molecules are inclined relative to the column axes at an angle of ~28°. An even more marked inclination has been observed in the columnar orthogonal mesophase D_{rd} of triphenylene hexahexyloxybenzoate, in the structure of which the molecular planes form an angle of about 40° with the column axes.[155]

The electrical conductivities of the CuPc metal complexes in the form of compressed discs (n = 8, 12) have been measured. Such measurements have become possible by virtue of the high viscosity of the mesophase, the conductivity of which increases with increase in temperature. On passing from the crystalline to the liquid-crystal state, a slight increase in the conductivity is observed: $\sigma_{n=8} = 5 \times 10^{-8}\ \Omega^{-1}\ m^{-1}$ and $\sigma_{n=12} = 7 \times 10^{-8}\ \Omega^{-1}\ m^{-1}$ at 175 °C. The activation energies for the mesophases of the above homologues E_a = 0.5–0.6 eV are appreciably smaller than for the unsubstituted crystal (R = H, $\sigma = 6 \times 10^{-8}\ \Omega^{-1}\ m^{-1}$, E_a = 1.4 eV). The measured difference can be explained by the fact[151] that a more effective overlap of the orbitals of the central parts of the molecules in the stacks occurs in the mesophase. We may recall that the central parts of the molecules in the mesophase are arranged at right angles to the stack axes, as a result of which there is an appreciable decrease in the forbidden gap between the valence and conductivity bands. This conclusion agrees with the measurements of the microwave conductivity with time resolution.[151]

It was noted above that the conductivities of the compounds CuPc with n = 8 and 12 are of the same order of magnitude. This demonstrates the independence of this property of the length of the alkyl chains. At the same time, the conductivity increases sharply after the introduction of electron-donating or electron-accepting compounds into these materials, because this leads to the appearance of free electrons or holes. Thus the addition of I_2 to CuPc (n = 8) in proportions of 1 : 1 by weight leads to an increase in conductivity by four orders of magnitude.[151] A gigantic increase in conductivity (by 9–10 orders of magnitude) compared with the initial MPc has been observed[156] in crystals of the nonstoichiometric compounds $MPcI_x$ ($x < 3$; M = Cu, Ni, Pt, Co, 2H). It is believed that the high conductivity is caused in this case by the incomplete oxidation of the MPc molecules within the stacks by the I_3^- anions, which results in the formation of 'holes'. Bearing in mind the fact that the conductivity of PcH_2I_x is of the same order of magnitude as that of the metal complexes $MPcI_x$, Peterson et al[156] concluded that the conductivity of these materials depends not so much on the metal–metal overlap as on the π–π or π–d overlap. This is attributed to the fact that the holes formed on partial oxidation can be concentrated either on the metal or on the ligand.

In the studies discussed, the conductivity was measured for powdered specimens and nonoriented mesophases, which naturally reduced its value. The small size of the CuPc (n = 8 and 12) single crystals and their acicular form, for which the molecular stacks are arranged along the long axis, made it impossible for the investigators to carry out measurements on single crystals. For comparison, we may point out that the conductivity of the single crystal specimen of (Qn) $(TCNQ)_2$, measured[157] at room temperature in the direction along the stacks ($\sigma = 10^4\ \Omega^{-1}\ m^{-1}$; $E_a \simeq 0$ eV), exceeds significantly the conductivity of the powder of this compound ($\sigma = 4 \times 10^2\ \Omega^{-1}\ m^{-1}$; $E_a \simeq 0.03$ eV).[158] We may note that an even greater conductivity in the direction of the chain axis has been observed for a single crystal of the Krogmann salt $K_2Pt(CN)_4Br_{0.30} \cdot 3H_2O$ ($\sigma = 3 \times 10^4\ \Omega^{-1}\ m^{-1}$).[159]

The phthalocyanine with R = $CH_2OC_{12}H_{25}$ forms a disordered hexagonal discotic mesophase D_{hd} with distances between the molecules in the columns of ~4.5 Å and a hexagonal lattice parameter of 31.2 Å.[148] The X-ray diffraction patterns of the mesophase show an additional intense reflection due to the periodic distortion of the columns with a wavelength of 20.5 Å. On the other hand, the copper complex of this compound forms an ordered mesophase D_{ho} in which the distance between the plane of the metallocycles is 3.8 Å and that between the columns is 34.0 Å.[147]

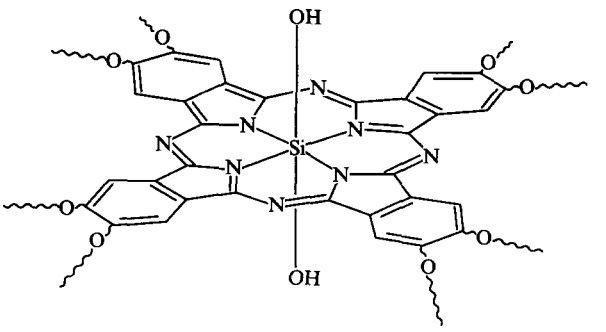
The introduction of other substituents into the phthalocyanine nucleus does not as a rule alter the columnar character of the mesophase formed, although the latter may be characterised by different structural types. For example, a series of polymorphic mesophases have been found for the copper complexes of phthalocyanine with chiral substituents R = $C_{12}H_{25}OC^*H(Me)CH_2OCH_2CH_2$, whereas the analogous complexes with nonchiral substituents form only one mesophase.[160] The influence of the length of the substituent on the type of mesophase has been investigated[161] for the copper complexes of phthalocyanine with R = $C_nH_{2n+1}OC_6H_4$ (n = 8, 10, 12, 18) and the analogous free nonmetallated phthalocyanines. For n = 12 and 18, the nonmetallated phthalocyanines form hexagonal phases with disordered columns D_{hd}, while the copper complexes form orthogonal phases D_{rd} (with $C2/m$ symmetry).

The copper complexes of phthalocyanines in which the substituents are crown-ethers, in particular 15-crown-5, are unusual. It has been suggested[162] that such molecules can form channels through which ions may be transported.

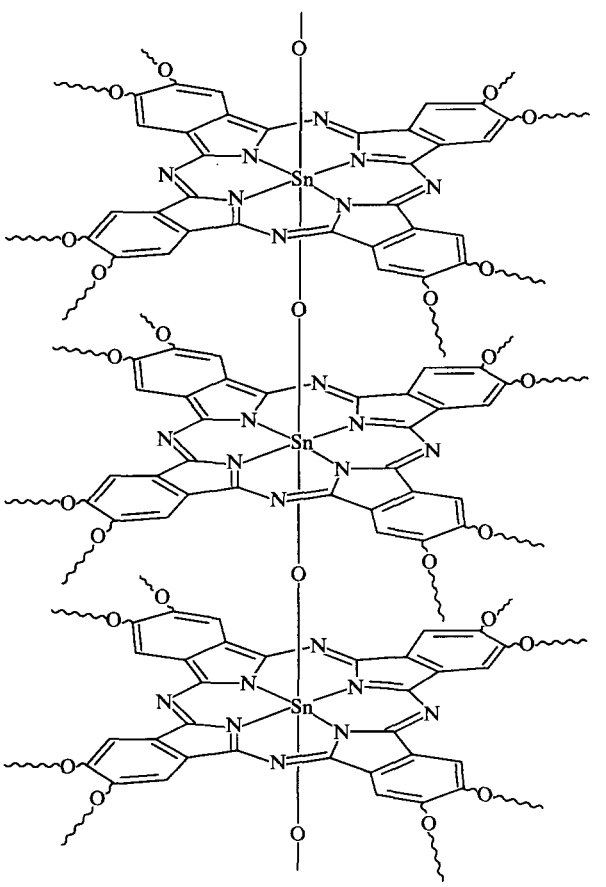
The complexes of phthalocyanines with other metals (Co, Ni, Pb, Zn, Mg) also form mesophases,[163-165] which, by virtue of their bright colour, have found extensive and varied applications.

Unusual discotic mesophases have been found[166-169] for two forms of bis(phthalocyanine)lutetium $Lu\{(ROCH_2)_8C_{32}H_8N_8\}_2$ ($LuPc_2$) with R = $C_{12}H_{25}$. It is emphasised that the red oxidised form, constituting a salt of the anion $SbCl_6^-$, is more stable than the green neutral form. X-Ray diffraction study of the $LuPc_2$ (R = $C_{18}H_{37}$) mesophase showed[7] that the distance between the columns is 37.0 Å, while the periodicity within the column (7.3 Å) is equal to twice the thickness of the phthalocyanine rings (Fig. 24). It is of interest that the form of the X-ray diffraction pattern at room temperature remains unchanged up to the transition of the isotropic phase, which indicates the similarity of the crystal and liquid-crystal structures. The conductivities of these phases are also approximately the same ($1.8 \times 10^{-7}\ \Omega^{-1}\ m^{-1}$ for the neutral form) and the probability of electron jumps within the columns is greater by a factor of 10^7 than the probability of the jumps between them for the same activation energy.

The phthalocyanine complexes in which the metal (Si or Sn) atoms are linked by oxygen bridges can be classified as liquid-crystal polymers. They are formed on heating from dihydroxy-complexes of the type:[170-172]

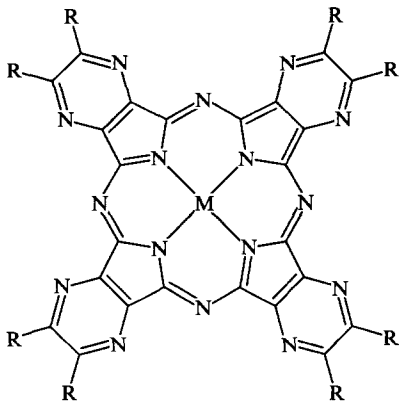


Bridged tin complexes form a columnar mesophase in the temperature range 59–114 °C, which is characterised[170] by a rectangular planar unit cell (25.2 Å × 30.7 Å) in which the distance between the metal atoms is 3.85 Å. The liquid isotropic phase of this compound is slowly transformed into a highly viscous anisotropic material, which contains polymer type bonds $(-O-Sn-)_n$ and a new temperature of transition to the isotropic phase (290 °C).



The analogous silicon phthalocyanine complex (n > 4) forms a hexagonal columnar mesophase of type D_{hd} in the temperature range from 20 to 300 °C. During heating in air at 180 °C, water evaporates, which is accompanied by the oligomerisation of the specimen to dimers, trimers, and higher oligomers.[171,172] We may note that a dimeric organisation of molecules, due to antiferroelectric pairing, has been observed in the phthalocyanine complexes of lead,[173] which form discotic mesophases with intercolumn distances of 26.9, 31.0, and 36.0 Å for R = $C_8H_{12}OCH_2$, $C_{12}H_{25}OCH_2$, and $C_{18}H_{37}OCH_2$ respectively.[174]

The synthesis and properties of substituted tetrapyrazinoporphyrazines and their complexes, similar to the phthalocyanine complexes, have been described.[175-177]



Discotic phases D_{rd} (with $C2/m$ symmetry) with an orthogonal centred cell and a disordered disposition of molecules in the column have been found for the complexes with M = Cu, Ni, or Co and R = $C_{12}H_{25}$. The similar phthalocyanine complexes have an analogous structure. The nonmetallated tetrapyrazinoporphyrazines form hexagonal columnar mesophases also with a disordered disposition of the molecules in the columns (D_{hd}). The compounds investigated are π-acceptor mesogenic substances. They are reduced more readily than the analogous phthalocyanine derivatives and this feature can be used to create discotic liquid crystals with mixed columns.

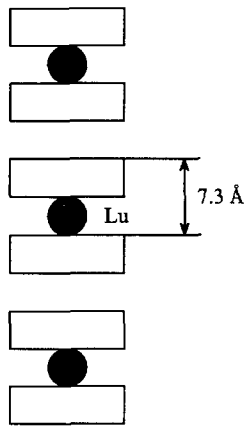
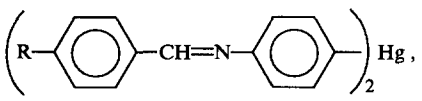


Figure 24. The structure of the columns in $LuPc_2$.

9. Organometallic and organoelement liquid-crystal compounds

Some of the first liquid-crystal compounds synthesised were organometallic mesogenic compounds. In particular, Vorländer obtained in 1923 the diarylmercury derivatives[7]

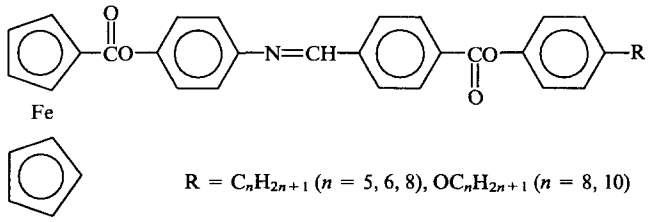


which exhibit smectic mesomorphism. The first example of a liquid-crystal π-complex (a ferrocene derivative) was described[178] in the middle 1970s. At the present time the number of studies devoted to such complexes is continually increasing. The first mentions of mesogenic materials belonging to the class of organoelement silicon derivatives were made at the beginning of the 1950s,[170,180] but such studies underwent a vigorous development only recently.

a. Ferrocene derivatives

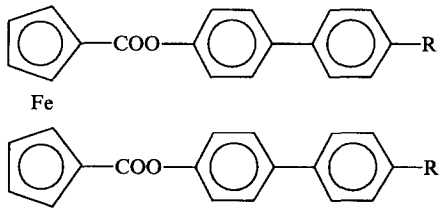
Ferrocene derivatives with Schiff bases as substituents are some of the first liquid-crystal smectic transition metal complexes obtained. They were synthesised by the reaction of the corresponding benzal-dehyde derivative with 4-aminophenyl-ferrocenyl carboxylate.[178]

Mesogenic ferrocene diesters, forming monotropic smectic mesophases,[181] were synthesised subsequently.[181]



R = C_nH_{2n+1} (n = 5, 6, 8), OC_nH_{2n+1} (n = 8, 10)

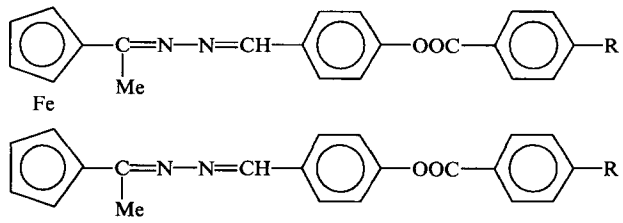
An X-ray diffraction study of one of these compounds (R = OC_5H_{11}) was carried out.[182] It showed that the molecule in the crystal occupies a specific position (at the centre of symmetry) and has a transoid form. The plane of the carbonyl group is coplanar with the plane of the cyclopentadienyl ring, but is almost perpendicular to the nearest benzene ring. The dihedral angle between the benzene rings (23°) is appreciably smaller than in the crystals[183,184] and mesophases[185] of various cyanobiphenyls.



R = OC_5H_{11}, C_6H_{13}.

Low-angle X-ray studies on the mesophase yielded little information compared with the study of the single crystals, which was attributed[182] to the thermal instability of the mesophase. However, for the homologue with R = C_6H_{13} it has nevertheless been possible to establish a layer periodicity (~47 Å) at the instant when the specimen consisted of a mixture of crystals and the mesophase. This quantity corresponds to an extended transoid molecular shape. Taking this factor into account and also the fact that in the crystal with R = OC_5H_{11} the molecule has the transoid form, the authors[182] concluded that the smectic phase contains precisely such molecules. It is emphasised that the bulky substituents in the mesogenic diesters prevent the torsional vibrations of the cyclopentadienyl rings around the C_5 axis.[186]

A nematic type of mesophase has been observed in the mesogenic series of compounds



R = OC_nH_{2n+1} (n = 1–8).

As in the case of the ferrocene diesters, the most probable form of these molecules is either U-shaped or S-shaped. In order to establish reliably the structure of the nematic mesophase of such compounds, a structural study was carried out[187] on a single crystal of 1,1′-bis[4′-(n-propoxy)benzoyl-4″-methyldiphenoxy-

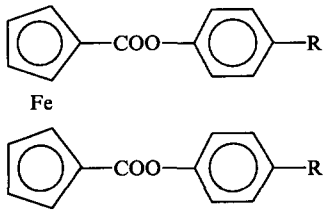
azinomethyl]ferrocene‡ (PBIFF, R = OC_3H_7), forming a mesophase in the temperature range 210–220 °C. Evidently, depending on the U- or S-shaped molecular structure, the nematic phase can be constructed in two ways (Fig. 25) within approximately the same characteristic periodicity of the mesophase ($d_1 \simeq d_2$) in both cases.

A molecule in the PBIFF crystal occupies a general position and has a U-shape in which the long axes of the ligands are almost parallel (Fig. 26). The conformations of two crystallographically independent ligands are similar; in each of them the carbonyl group is coplanar with one benzene ring [C(16)–C(21)] and has rotated by approximately 50° relative to the plane of the other ring [C(9)–C(14)], the planar fragments of one ligand being parallel to the analogous fragment of the other.

In the crystal (Fig. 27), the molecules are packed in an antiparallel arrangement, forming layers, and an interpenetration of the ferrocene component of the molecules from one layer into the other is observed. Despite the layered character of the packing, [the layers are energetically appreciably less distinct ($U_{layer}/U_{interlayer} \simeq 2.8$) than in the metal complexes of Schiff bases], the contacts between the rigid ferrocene components of the molecules rule out the possibility of the formation of a smectic mesophase, because such layers cannot slide freely relative to one another. On the other hand, the antiparallel arrangement of the molecules does not conflict with the structure of the nematic phase. The investigation described[187] permits the conclusion that the nematic phase of PBIFF consists of cisoid molecules. The presence in the crystal of energetically indistinct layers agrees with X-ray diffraction studies on mesophases of this series,[188] from which it follows that the molecules in the nematic phase can form small lamellar associated species.

We may note that the S-shape of the mesogenic ferrocene molecules is more favourable than the U-shape for the formation of the smectic mesophase, since mobile alkyl substituents would be involved in the interlayer contacts on either side for this shape. Conformational calculation carried out for disubstituted ferrocenes showed[187] that the U-shape is more favourable for an isolated molecule, whereas in the crystal and in the mesophase the energies of the U- and S-shaped forms may be similar when account is taken of the nonvalence intermolecular interactions.

Yet another series of ferrocene derivatives



with R = OC_7H_{15}, $OC_{10}H_{21}$, OH, and OCH_2Ph has been described.[189] For R = OC_7H_{15} and $OC_{10}H_{21}$, the compounds form a nematic phase, the phase of the compound with R = OH being characterised by the largest temperature range (hydrogen bonds can probably be formed under these conditions). For the homologue with R = OCH_2Ph, a mesophase is not formed.

b. Organoelement liquid crystals

The majority of the thermotropic mesophases known at the present time are made up of molecules having an anisometric shape — rods or discs. At the same time, data are being published with an increasing frequency concerning the formation of mesophases by compounds the molecules of which do not possess the classical anisometry. The unusual mesophase formed by one of the representatives of the series of silanediols $R_2Si(OH)_2$

‡ 1,1′-Bis[*p*-(*p*′-n-propoxybenzoyloxy)benzylidenehydrazono(α-ethyl)]-ferrocene? [Translator].

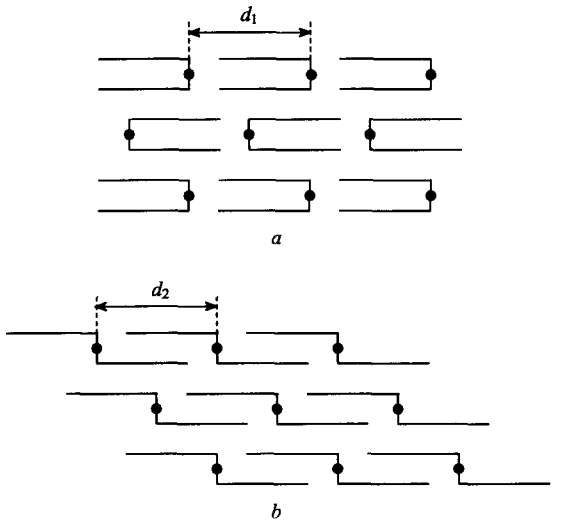


Figure 25. The structure of the cisoid (*a*) and transoid (*b*) molecules in the nematic mesophase of disubstituted ferrocene.[187]

(R = Bu^i) — diisobutylsilanediol (DISD) — may be included among them.[179,180]

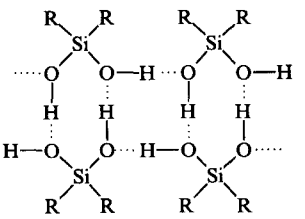
As early as 1952, the unusual behaviour of DISD on fusion was noted.[179] It is due to the existence of a mesophase in the temperature range 89.5–101.5 °C. For other derivatives of this series with R = Me, Et, Ph, Pr^i, or Bu^t, the manifestation of mesomorphism was not observed.[179,180] The DISD mesophase was initially identified as smectic, consisting of extended chains of hydrogen-bonded molecules. The accumulated data on the structures of liquid crystals and especially the discovery of discotic mesophases[1] made it necessary to return to the investigation of the structure of this unusual mesophase after almost 30 years.[190]

Calorimetric study of DISD demonstrated the similarity of the enthalpies of the phase transitions

$$C \xrightarrow[7.6\ kJ\ mol^{-1}]{89.5\ ^\circ C} LC \xrightarrow[7.2\ kJ\ mol^{-1}]{101.5\ ^\circ C} IL.$$

According to Bunning et al,[190] this shows that only some of the hydrogen bonds present in the crystal are disrupted in the first phase transition, while some remain and are disrupted only on transition to the isotropic liquid. We may note that discotic mesophases, where there are no hydrogen bonds, are also characterised by similar enthalpies of the phase transitions C → LC and LC → IL.[54] It has been emphasised[190] that the textures of the DISD mesophase resemble those of discotic materials and their continuous miscibility with a classical discotic compound, namely hexa(n-heptyloxy)benzene, has been observed.

The X-ray diffraction patterns of the DISD mesophase contain[190] two diffuse rings corresponding to interplanar distances of 4.7 and 11.0 Å. The crystal structure of this compound has not been established, but the parameters of a nearly hexagonal triclinic cell with $a \simeq 12$ Å have been found. It has been possible to carry out a structural study on single crystals for a



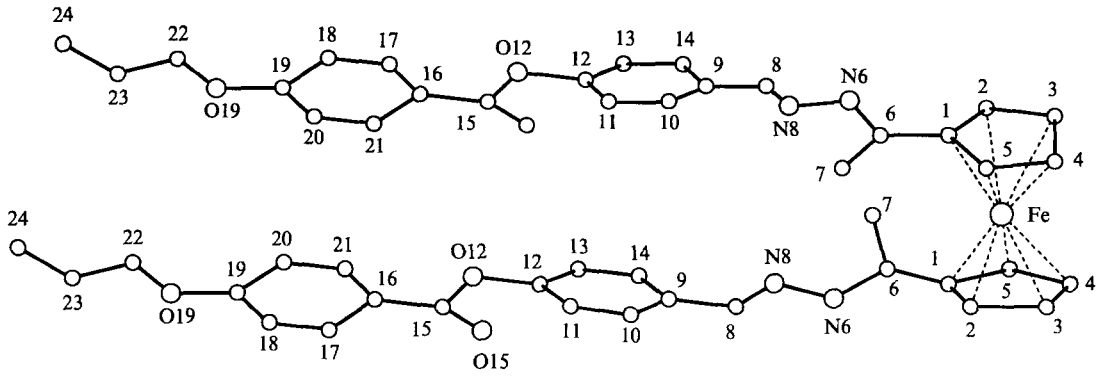


Figure 26. The structure of the PBIFF molecule.

series of DISD homologues.[191-193] Thus hydrogen-bonded strips made up of dimers have been observed for crystals with R = Pr^i and Bu^t.

On the basis of the above data, it was concluded[190] that the DISD mesophase is discotic. The role of discoid molecules is assumed in this case by the hydrogen-bonded dimers. In the DISD crystal, these dimers are joined together by hydrogen bonds into inclined stacks (Fig. 28) with an approximately hexagonal arrangement. It is believed that during heating, in the transition of the crystal to the mesophase, the interdimer hydrogen bonds are broken, while the intradimer hydrogen bonds are retained. However, it is noteworthy that the latter requires significant evidence, since it is not entirely clear why selective and not random dissociation of hydrogen bonds takes place (in crystals with R = Pr^i and Bu^t, all these bonds have virtually the same lengths and hence similar energies).

In the related series of lower-melting disiloxanediols,[194] thermotropic mesomorphism proved to be a more general property. It has been observed for compounds with alkyl substituents having the normal structure (R = n-C_nH_{2n+1}, n = 2–4), but not for compounds with R = Me, Ph, or isoalkyl.

The results of X-ray diffraction studies on single crystals and mesophases as well as IR spectroscopic, calorimetric, and optical studies on compounds of the class of DISD and its analogues have been surveyed,[5,6,195-197] which has made it possible to characterise fairly fully the mesophases examined and to assign them to a new structural type.

The crystal structures of three nonmesogenic and two mesogenic compounds of the DISD series are now known. Studies have shown that 1,3-dihydroxy-1,1,3,3-tetraalkyldisiloxanes (DTADS), namely DTPDS (R = Pr^n),[195] DTMDS (R = Me),[6] DTEDS (R = Et),[197] and DTPDS (R = Ph),[198] have the same molecular packing in the crystals and the same system of intermolecular cooperative hydrogen bonds, without dimeric organisation, regardless of the fact that their crystals belong to different structural classes.

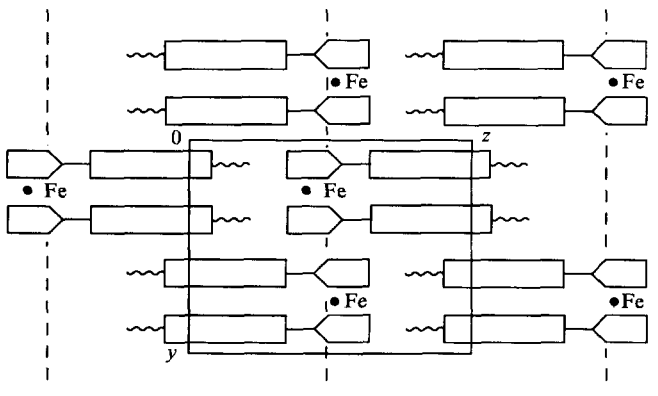
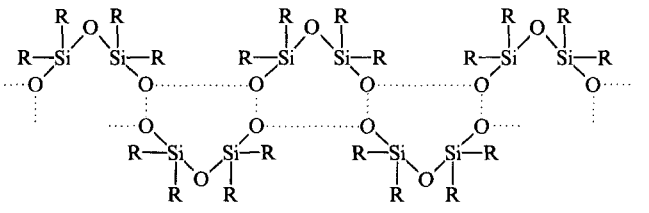


Figure 27. The layered packing of the molecules in the PBIFF crystal. The layer boundaries are shown dashed.[187]



The system of hydrogen bonds in the DTMDS crystal can be described as two chains of hydrogen-bonded molecules linked by transverse hydrogen bonds into infinite strips with 2_1 symmetry and extended along the b axis (Fig. 29). In contrast to DTMDS, the crystal of which contains one system of independent molecules, in the DTPDS crystal the analogous strips are formed by six independent molecules A–E (Fig. 30), while in DTEDS

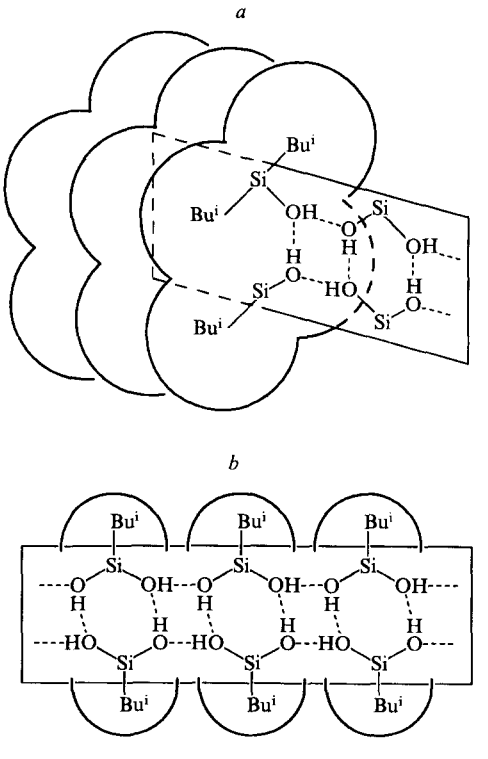
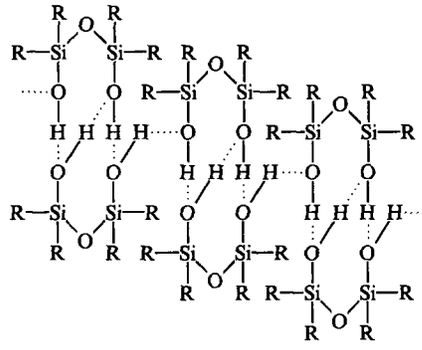


Figure 28. The structure of the dimeric discotic DISD phase: (*a*) perspective view along the column; (*b*) view at right angles to the column.

centrosymmetric hydrogen-bonded strips are formed by two independent molecules. Similar strips are observed also in the DTPDS crystal, but here they are made up of three symmetrically independent molecules. In the majority of the crystals which we examined there are conformational differences between symmetrically independent molecules, which is indicated by the differences between the SiOSi bond angles and the pseudotorsional (H)SiO ... OSi(H) angles characterising the overall molecular conformation.

In the crystal of the isopropyl homologue of DTPDS, i.e. Pr^i_2(OH)SiOSi(OH)Pr^i_2, the hydrogen bond system is somewhat different, although here too strips of hydrogen-bonded molecules are observed.[199]



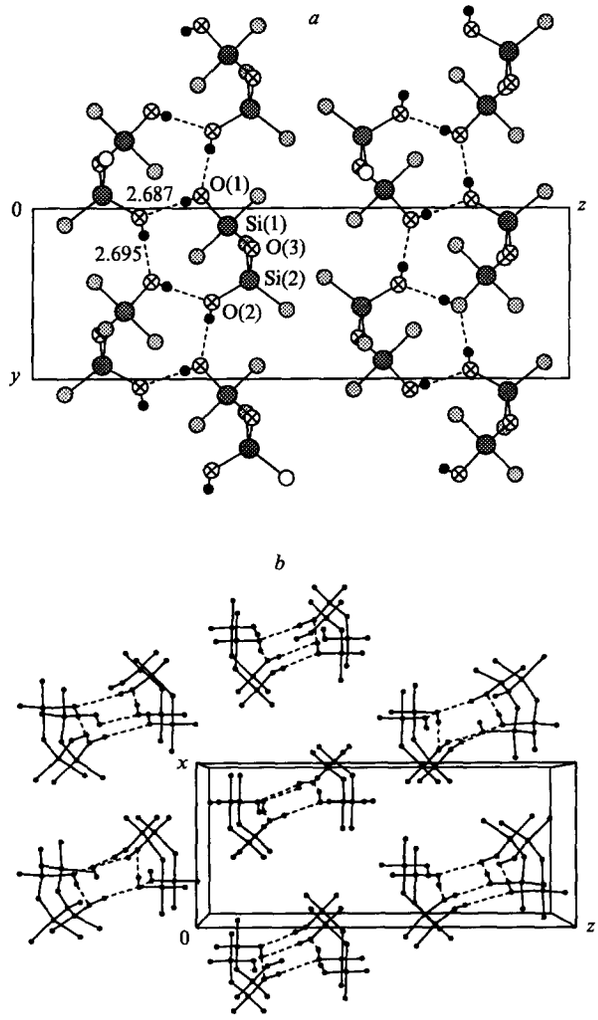


Figure 29. Projection of the crystal structure of DTMDS onto the *yz* (*a*) and *xz* (*b*) planes:[6] (*a*) view at right angles to the column; (*b*) view along the column.

In this structure, made up of two crystallographically independent molecules, three out of the four hydrogen bonds combine the molecules into dimers whilst the fourth hydrogen bond combines the dimers into strips.

The shape of the molecular strips in the structures of disiloxanediols, considered along the long axis, i.e. the crystallographic *b* axis (Fig. 30), is of great interest. These strips are approximately cylindrical, the surface layer of the quasi-cylinders, especially in the Pr^n and Et homologues, being framed by conformationally flexible alkyl substituents. The alkyl environment of the quasi-cylindrical strips (columns) is very similar to that in columnar discotic mesophases.[2] The similarity of the alkyl frame around the quasi-cylindrical strips in the crystal to the structure of the columns in the mesophase is manifested by the presence in the crystal of several independent molecules with different conformations of the alkyl substituents and by the lack of order in the arrangement of these substituents.

The quasi-cylinders formed by hydrogen bonds in the crystals of three alkyl homologues are arranged pseudohexagonally in the *ac* plane. The parameter of the planar pseudohexagonal unit cell in the crystal is a = 12.66 Å for DTPDS and a = 10.69 Å for DTEDS. According to X-ray diffraction studies on the mesophases of the corresponding compounds,[194] the parameters of the planar hexagonal unit cells are 12.58 and 11.10 Å, i.e. are close to those observed in the crystal. The hexagonal type of the cells and the similarity of the parameters permit the conclusion that the crystalline and liquid crystal phases in DTPDS and DTEDS are structurally continuous. The diffractometer trace for the Bu^n derivative (DTBDS), the structure of the single crystal of which could not be investigated, indicates that its mesophase also belongs to the hexagonal type.

The characteristic features of the textures of the mesophases of the compounds DTEDS, DTPDS, and DTBDS have been investigated.[5] It was shown that they resemble the textures of the hexagonal columnar discotic phases.[200,201] A model of the structures of DTEDS, DTPDS, and DTBDS, similar to the structure of the DISD mesophase in which the hydrogen-bonded dimers play the role of discoid units and their assembly forms the column, was proposed initially.[194] However, the crystal structures of the homologues investigated suggested another model, namely

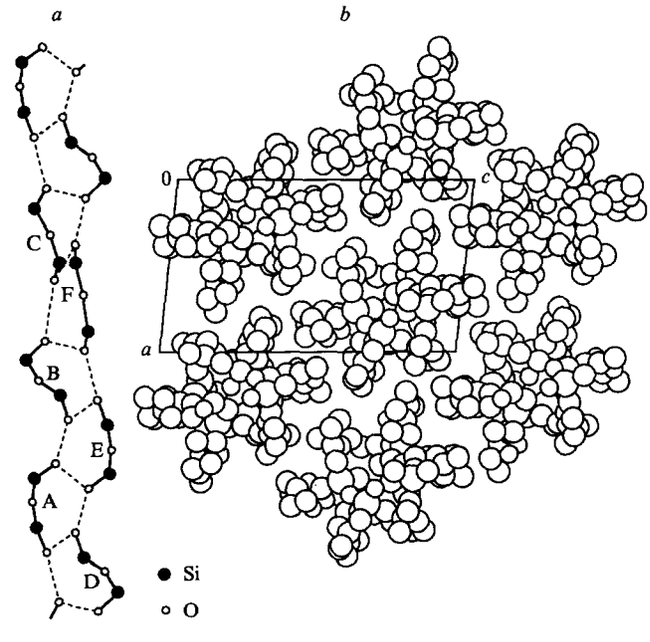
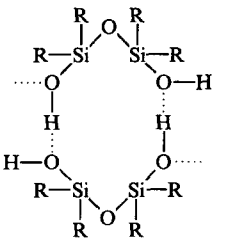


Figure 30. Projection of the crystal structure of DTPDS onto the *bc* (*a*) and *ac* (*b*) planes: (*a*) view at right angles to the column; (*b*) view along the column. The arrangement of the quasi-cylindrical molecular columns is pseudohexagonal.[196]

the presence in the mesophases of columns of hydrogen-bonded molecules (observed in crystals) and not of dimers.



Spectroscopic studies[5,196] have demonstrated the retention of a considerable number of 'crystalline' hydrogen bonds in the mesophase, i.e. in the crystal → liquid-crystal phase transition columns of hydrogen-bonded molecules, present in the crystals, may be retained. Furthermore apart from the similarity of the parameters of the hexagonal cells, the similarity between the crystal and liquid-crystal structures of disiloxanes was demonstrated by optical measurements of the refractive index along and at right angles to the columns. It was found that $n_{\parallel} < n_{\perp}$ both in the DTPDS crystal and in the mesophase.[5] Naturally, in contrast to the crystals, in the liquid-crystal state these columns have finite and different lengths and there is no translational order along their long axes, but there is a certain long-range orientational order. In the perpendicular direction, the long-range translational order is manifested by the occurrence of a planar hexagonal cell.

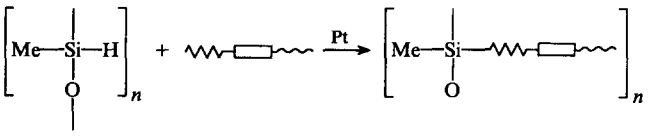
The absence of mesomorphic properties from the Ph and Me homologues is due to the fact that in DTPDS the outer layer of the column is made up of the rigid Ph substituents, while in DTMDS the surrounding layer of alkyl groups is minimal. The absence of the mesophase from diisopropyldisiloxanediol can be explained by the fact that in this case there is no infinite system of hydrogen-bonded molecules but dimers connected by hydrogen bonds do exist.

In our view, the DTEDS, DTPDS, and DTBDS mesophases, made up of molecular columns constructed as a result of the formation of cooperative hydrogen bonds and surrounded by alkyl substituents, should be assigned to a new structural type of liquid crystals. This type has been called[5,6] 'mesophases with columnar hydrogen-bonded associated species', since such liquid-crystal phases differ significantly in the mode of their formation both from phases made up of rod-shaped molecules and phases constructed from discoid molecules. The DISD mesophase can also be assigned to this class, because it is more likely that, in the transition to the liquid-crystal state, the hydrogen bonds are ruptured at random and the mesophase is formed not so much by free dimers or other associated species (for example trimers)¶ as by columns formed by hydrogen bonds.

c. Cyclic siloxanes

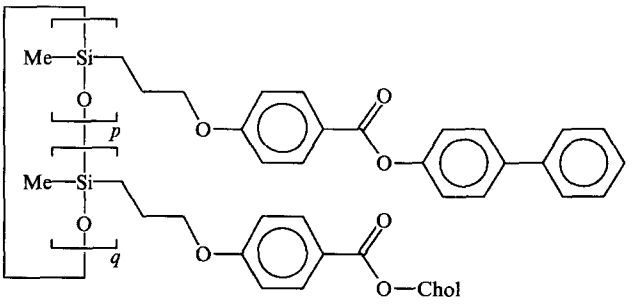
There exist many data on the mesomorphism of polylinear siloxanes. The mesomorphic properties of these polymers are manifested both in the presence[202,203] and absence[204,205] of mesogenic side substituents.

Low-molecular-mass cyclic siloxanes with mesogenic substituents, exhibiting liquid crystal properties, were obtained at the beginning of the 1980s.[206] One of the methods of synthesis of such compounds is hydrosilylation of cyclic siloxanes in accordance with the scheme[207]



¶ J E Lydon, personal communication.

Derivatives of biphenylenes, esters, and cholesteryl (Chol) benzoate can be used as substituents. In a number of instances derivatives with substituents of two types are also possible.



Even small siloxane rings are appreciably flexible.[208] This makes it possible to postulate that, although the mobility of the long mesogenic substituents in the molecules of cyclic siloxanes is limited by their incorporation in a ring, it does have sufficient degrees of freedom. Computer modelling showed that such molecules can have different configurations and can form both discotic and nematic phases.[209]

The study of the phase state of the cyclic siloxanes with the ring sizes $p+q = 4-7$[207] and 4–24[210] demonstrated the presence of mesophases of the nematic and smectic types for these compounds. The properties of such mesophases depend both on the number of chain units and on the dimensions of the side substituents. For example, virtually no change in the thickness of the layers with increase in the size of the ring is observed for type SmA mesophases with the same side substituents.[207]

X-Ray diffraction studies on the mesophases made up of siloxane rings with two types of substituents showed that they possess a high degree of order. In the analysis of the structure of a type SmA mesophase, three types of molecules were considered:[211] discotic, cylindrical, and conical (Fig. 31), and it was concluded that the cylindrical type is most likely. It has been noted that the thickness of the layer is usually determined by the

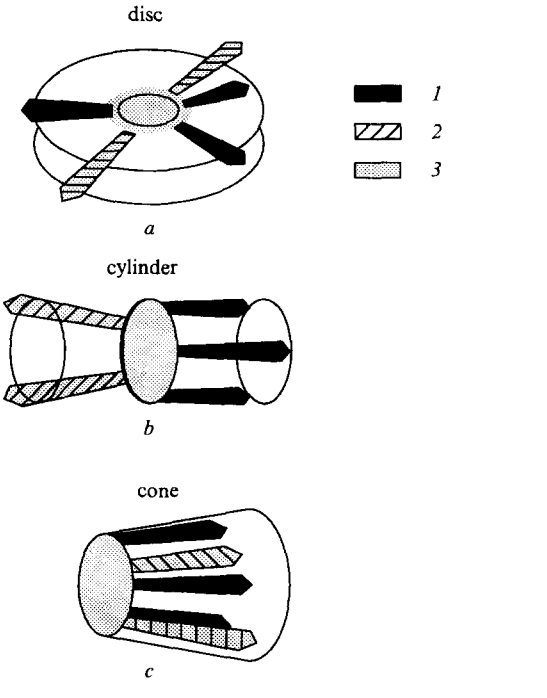


Figure 31. Molecules made up of cylindrical siloxanes with two types of substituents.[213] Molecules: (*a*) discotic; (*b*) cylindrical; (*c*) conical; (*1*) biphenyl nuclei; (*2*) cholesteryl nuclei; (*3*) cyclic siloxane.

length of the large substituent and can change when the ratio of the substituents $p:q$ in the ring is altered.[211] According to the results of optical studies, the layers in smectic specimens have a helicoidal twist (Fig. 32). The latter factor and also the tendency of the above compounds to vitrify create good prospects for their application in optical systems.

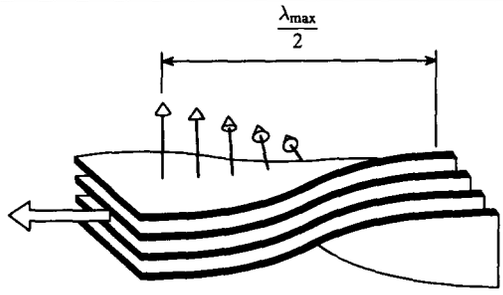


Figure 32. Helicoidal twisting of the smectic layers in cyclic siloxanes.[213]

IV. Conclusion

The above analysis of the literature and the authors' own data permits certain conclusions concerning the structural aspects of metallomesogenic substances. Despite the fact that metal complexes have not been investigated as extensively as classical organic liquid crystals, nevertheless one may say that, as in the case of organic liquid crystals, for the manifestation of mesomorphism the molecules of metal complexes must possess either intrinsic anisometry or they must form anisometric associated species the shape of which may differ significantly from that of the initial molecules. The discotic mesophases of β-diketones, made up of extended molecules, may serve as an example. Special mention should be made of the fact that in metal complexes the anisometry of the molecule depends significantly on the coordination of the metal atom, which has been manifested most clearly in the complexes with Schiff bases.

The presence of additional intermolecular coordination can have a dual effect on the mesomorphic properties. If this coordination leads to the formation of anisometric associated species, for example, columns in columnar phases, mesomorphism is possible. However, in the majority of cases such coordination plays a negative role, because the coordination dimers, strata, etc. are as a rule characterised by a lower anisometry. The EPR spectra of copper complexes of Schiff bases indicate unambiguously the absence of additional coordination in the mesophase.

In ionic liquid crystals, the smectic mesomorphism is due to the bilayer nature of the ordering of the molecules in which the metal and oxygen atoms within the bilayer form cation–anion strata separated by layers of alkyl substituents. It is of interest that in the strata the metal atom is located between oxygen planes and that water molecules are involved in the formation of such planes in the structure of, for example, $Cd(Isoval)_2 \cdot 2H_2O$. Apparently this is the first compound in which the presence of water molecules determines the appearance of the liquid-crystal state.

The mesophases based on silanediols are a striking example of the dependence of the mesomorphism on the type of aggregation of the molecules. The unusual feature of these substance consists in the fact that their molecules, which have no anisometry, form columnar associated species via hydrogen bonding, which give rise to hexagonal mesophases. The completely new structure of these mesophases (mesophases with columnar hydrogen-bonded associated species) is in many respects determined by the conformational flexibility of the molecules.

Finally, we may note that X-ray diffraction data for single crystals are very useful for the understanding of the relationship between the structure of the molecules and their ability to form liquid crystals. Such studies make it possible to determine reliably the molecular and crystal structures and then to extrapolate them to the mesophase in which the principal features of the crystal structure (layers, columns, coordination of the metal atoms, etc.) are retained. As regards the practical use of the compounds examined in this review, the prospects for their application have already been outlined.[7] We only wish to note the ability of ionic liquid crystals to form stable anisotropic glasses, which can be used for various spectroscopic purposes.

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