Chem. Rev. 1993, 93, 861–885

Calamitic Metallomesogens: Metal-Containing Liquid Crystals with Rodlike Shapes

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Received August 10, 1992 (Revised Manuscript Received December 16, 1992)

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I. Introduction

Interdisciplinary topics frequently herald great advances in science. Metal-containing liquid crystals, which we have termed "metallomesogens", combine the physical characteristics exhibited by metal coordination complexes with those of organic molecules which give liquid crystals. Such compounds were first made over 80 years ago but the topic has achieved a distinctive character only recently (see ref 1). This present review, covering the literature to the end of January 1992, concentrates on calamitic (rod-shaped) thermotropics (liquid crystals which change phase with heat) and emphasizes developments which have occurred since the beginning of 1990. For completeness, selected references are included to the earlier literature but the reader is referred to the previous review[1] for more detail.

Although most of the classical studies of liquid crystals have involved organic materials, when the organic molecules contain heteroatoms able to bind to metals, they can function as ligands which stabilize metal complexes as liquid crystals. In broad terms this means that the dipole–dipole and dispersion forces which hold liquid crystals in anisotropic supramolecular arrays, are not destroyed by the introduction of the metals. Indeed in some cases the mesophases found are identical to those exhibited by the pure organic ligands themselves.

The scope for metallomesogens is great, as there are some 60 metals which can in principle be coordinated to organic ligands. Metals also show a remarkable variety of geometries in addition to the linear, trigonal, and tetrahedral coordinations exhibited by carbon, and the incorporation of a metal immediately opens up a wide choice of new geometric shapes. Further important effects arise from the large and polarizable electron density which is a feature of every metal atom and, since many metal ions of the d and f block elements have unpaired electrons and are colored, their inclusion opens up the possibilities of the incorporation of new physical properties into the liquid crystals.

A. Definitions

Liquid crystals form a state of matter intermediate between the solid and the liquid.[2] The terms mesomorph (Greek, mesos morphe, between two states, forms) and mesophase are also used; a mesogen is the molecule which gives rise to a mesophase. Liquid crystals can broadly be divided into thermotropics and lyotropics. Thermotropic liquid crystals change phase with temperature; the crystals melt to the mesophase (at the melting point) and then clear to the isotropic liquid at a higher temperature; this is termed the clearing point, reflecting the fact that mesophases often appear turbid while the isotropic liquid is clear. Some show several mesophases; they exhibit polymorphism. Lyotropic phases are formed by molecules in a solvent (generally water), and the appearance of the mesophase is controlled by the concentration as well as the temperature. Few lyotropic metallomesogens, other than those of the alkali metals, have yet been made.

A crystal (denoted by K or C) has a defined shape, and (except for cubics) most of its physical properties are anisotropic because the constituent molecules or ions are ordered in position and orientation. By contrast, the component molecules (or ions) of a fluid lack positional and orientational ordering; hence the physical properties are isotropic (I). In a thermotropic mesophase varying degrees of positional order are lost, giving a fluidity, while orientational (supramolecular) order is retained, giving the anisotropy. A consequence of this anisotropy is that mesophases can have two (or even three) different refractive indices, magnetic susceptibilities, and electric permittivities. As a result, some thermotropic molecules can be oriented by applied

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Sarah Hudson was born in Beirut, Lebanon, in 1964. She received her degree from the University of Wales, Aberystwyth, in 1988, having spent one year of her degree course working on antiviral products with Beecham's Pharmaceuticals. Her Ph.D. studies at Sheffield University with Drs. D. W. Bruce, D. A. Dunmur and Professor Maitlis were in the field of metallomesogen chemistry, concentrating on the silver(I) complexes of stilbazoles. She is currently carrying out postdoctoral studies on organometallic chemistry involving nickel and palladium at the University of Sevilla, Spain, with Professor Ernesto Carmona.

After obtaining his Bachelor's degree from Birmingham University and his Ph.D. degree from London University, Peter Maitlis stayed on at Queen Mary College, London, as Assistant Lecturer before crossing the Atlantic as Fulbright Fellow, first at Cornell and then at Harvard. He was on the staff at McMaster University, Hamilton, Ontario, Canada, for 10 years, before returning to England in 1972 as Professor of Inorganic Chemistry at the University of Sheffield. He was an Alfred P. Sloan Fellow and won the E. W. R. Steacie Prize, while in Canada, as well as the Sir Edward Frankland Prize Lectureship of the Royal Society of Chemistry, after his return to England. In 1984 he was elected to the Royal Society, where he is currently serving on the Council. He is scheduled to be the next Pacific West Coast Lecturer (in Canada and the United States) later this year. His main research interests are in the interaction of transition metals with organic compounds, where he has made many contributions to synthesis, reaction mechanisms, and catalysis. This work has more recently been extended to the development of the chemistry of metal-containing liquid crystals, the topic of the present review.

electric or magnetic fields; this is the basis of their considerable practical applications.

Figure 1. Schematic representation of a nematic (N) calamitic phase.

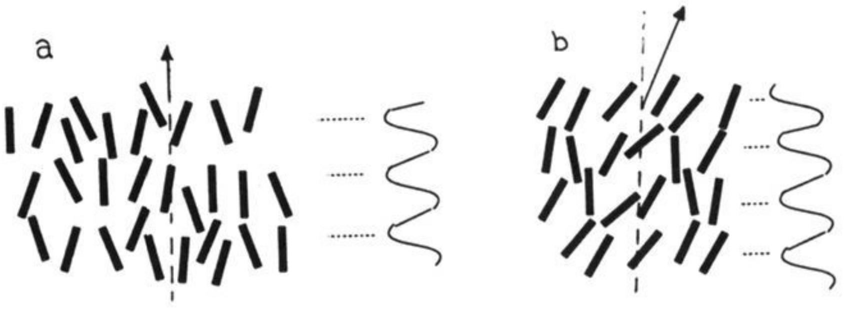


Figure 2. (a) Schematic representation of a smectic A (S_A) calamitic phase and (b) schematic representation of a smectic C (S_C) calamitic phase.

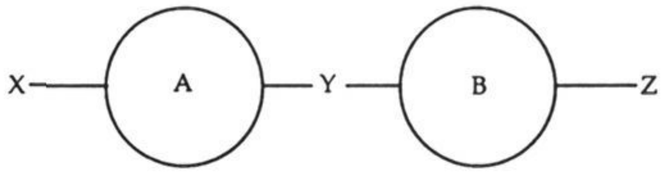


Figure 3. Schematic representation of a calamitic (rodlike) molecule.

Thermotropics can be further subdivided into calamitic (rodlike) and discotic (disklike, denoted by D); rodlike thermotropics are classified as nematics (N) and smectics (S). In the least ordered phase, the nematic, the rodlike molecules line up approximately parallel to each other (Figure 1); along a direction defined by the director, *n*. The transition from the crystalline to the nematic phase (K → N) is often associated with an enthalpy change about 10 times higher than the nematic to isotropic (N → I) transition. The introduction of a chiral center into a nematic molecule gives rise to cholesteric behavior, where the director is now helical.

Smectic liquid crystals form a variety of layered phases, which offer additional order over that found for nematics; some have phases with the molecules perpendicular to the layers (e.g., S_A; Figure 2a), in others they are inclined to them (e.g., S_C; Figure 2b). It should be remembered that the mesophase structures are not static, and each representation is a snapshot; for example, smectic layers can be described by one dimensional density waves. Discotic liquid crystalline phases are obtained with disklike molecules where the director is perpendicular to the molecular plane; discotic metallomesogens have been reviewed[1] and are not included here.

Organic compounds that exhibit calamitic liquid crystalline properties contain a long rigid core, often made up of aromatic rings (A and B in Figure 3), connected by linking groups (Y, e.g. $—CH_2CH_2—$, $—CH{=}N—$, $—CH_2O—$, or $—COO—$), and end groups (X,Z), of which X (and sometimes Z as well) will be a long flexible *n*-alkyl (or *n*-alkyloxy) tail. The other end group (Z) is frequently a polar function such as a nitrile. The resulting rodlike polarizable core, together with the flexible end chains, increase the molecular anisotropy, and facilitate liquid crystal formation.

The magnitudes of the weak dipole–dipole and dispersion forces which hold thermotropics together are critical: when they are too weak or when they are too strong, the liquid crystalline character is lost. Hence the molecular features which optimize thermotropic behavior are very important.

The characterization of thermotropic mesophases relies initially on optical microscopy; as the temperature is changed the different phases show characteristic textures when viewed between crossed polarizers.

Mixing with a known mesophase will often confirm the assignment, since two identical mesophases are normally miscible. Further confirmation and assignment require differential scanning calorimetry (DSC), and low-angle X-ray scattering in the mesophase.

Data on liquid crystals are often presented as two-dimensional phase diagrams, where the phase transition temperatures (y axis) are plotted against a structural parameter (x axis), usually the number of carbon atoms in the flexible tail. This is a convenient way to show the different enantiotropic (thermodynamically stable) phases and their stabilities, the presence of monotropic (thermodynamically unstable) phases, and the effect of change of tail length on phase type and transition temperature. A typical phase diagram will often show that shorter tails give rise to nematic and longer to smectic phases and also often indicates an alternation of transition temperatures with increase in tail length. A typical example of a phase diagram is included in Figure 16. A three-dimensional phase diagram is shown in Figure 11 where the temperatures are plotted against the lengths of both the terminal (x axis) and the lateral chains (z axis).

B. Historical

In 1910 Vorländer[3] discovered that the alkali metal carboxylates, $R(CH_2)_nCOO\ Na$, formed classical lamellar phases characteristic of soaps. Later, in 1923, he also found that the diarylmercury Schiff bases ($(RC_6H_4CH{=}NC_6H_4)_2Hg$) form smectic phases.[4] Other alkali and alkaline earth salts of carboxylic acids with organized mesophases were characterized by Skoulios and his collaborators,[5] while the smectic ferrocenyl Schiff bases ($C_5H_5FeC_5H_4CO_2C_6H_4N{=}CHC_6H_4O_2CC_6H_4X$; $X = C_nH_{2n+1}$ or OC_nH_{2n+1}) were synthesized by Malthête and Billard in 1976.[6] Giroud and Müller-Westerhoff in 1977 reported the mesogenic nickel and platinum dithiolenes[7] and were the first to seek advanced materials (novel substances for electronic, optoelectronic, and related applications) among such compounds.

Because mesophase formation depends on intermolecular forces and because much of the space around the metal is occupied by the ligand, the properties of metallomesogens are, to a first approximation, dominated by the ligands and their arrangement, in other words by the overall shape of the molecule. Thus, for example, long monodentate ligands (or bidentate ones with small bite angles) will tend to give rodlike nematics and smectics, while flat, disklike polydentate ligands (for example, macrocycles) will give discotics. A relatively small number of ligand types have tended to dominate the field of rodlike metallomesogens so far, for example, cyanobiphenyls or 4-stilbazoles (for silver, palladium, and platinum), salicylaldimines (for copper and nickel), and the orthometalated imines and azines (for palladium). However, the very recent development of new ligand systems suggests that mesophases will not be restricted to calamitics or discotics and that intermediate situations are also possible.

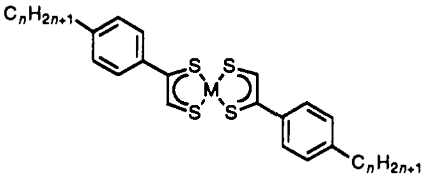
X-ray diffraction studies suggest that in the crystalline state many metallomesogens have interactions which enable the metal to interact axially (although weakly) with a donor atom on a neighboring molecule, and this feature appears to have an important, if as yet unquantified, bearing on mesophase formation.

In this review calamitic metallomesogens have been arranged by metal, starting with nickel, palladium, and platinum (as this group contains molecules of very simple square planar d^8 geometry), and then proceeding to copper(II), which has a large number of liquid crystalline complexes, again with a basically square-planar stereochemistry. This geometry is also found for mesomorphic gold(III), rhodium(I), and iridium(I) complexes, while silver(I) mesogens show modified linear coordination, and vanadium (vanadyl, VO^{2+}) and some zinc complexes are square pyramidal. The remaining elements, iron, cadmium, mercury, lead, the alkali, the alkaline earth, and the rare earth metals, where rather few examples are yet known, show a variety of geometries, including some which are effectively 6-coordinate. The alternative organization, by ligand type (i.e. shape) was adopted for the earlier review;[1] the two aspects thus offer a stereoscopic view of the whole area.

II. Group 10: Nickel, Palladium, Platinum

A. Nickel

Nickel(II) (d^8 electron configuration) is the only oxidation state where liquid crystalline compounds have so far been reported. Square-planar, tetrahedral, 5-coordinate, and octahedral geometries are known for Ni(II). All the mesomorphic complexes are diamagnetic, which has been interpreted to indicate a square-planar coordination about the metal. However, complexes with square-pyramidal or trigonal-bipyramidal geometries would also be diamagnetic; thus, for example, a square-planar arrangement with an axial interaction should also be considered. The first mesogenic nickel complexes (which have already been discussed[1]) were the calamitic dithiolenes, 1 (M = Ni), made by Giroud and Müller-Westerhoff in 1977.[7] More recently attention has focused on the rather easier of access salicylaldimine and dithiobenzoate complexes.

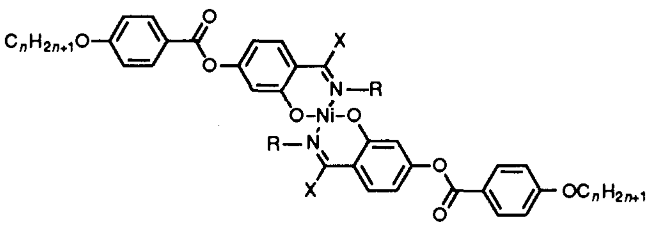


1: M = Ni, Pt

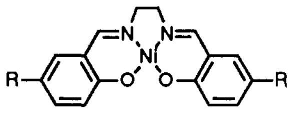
1. Salicylaldimines

The salicylaldimine complexes **2** made by Serrano and his colleagues in Zaragoza,[8] showed smectic phases; since they were diamagnetic, they were assigned a square-planar coordination about Ni(II), similar to that of the copper(II) analogs (section III.A). The complexes based on *p*-alkyloxyanilines gave nematic mesophases for short alkyloxy chains.[9] Gray and collaborators (and Shaffer and Sheth), found that the bis(salicylidene)-ethylenediamine complexes **3** exhibited high melting S_A phases.[10]

The complexes **4**, related to **2**, using the *N*-(*n*-propyl)-salicylaldimine ligands reported by Hoshino et al.,[11] all showed nematic phases. They had the unusual feature that, while the shorter chain length complexes (n = 4–12) showed enantiotropic liquid crystalline phases, on lengthening the tail to n = 14, 16, and 18, the nematic phase became monotropic. ^1H NMR spectroscopy of **4** (n = 11) in the nematic phase showed that it was ordered normally. The ^1H NMR solution spectra were

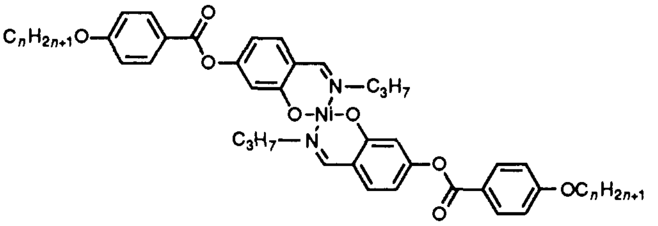


2: X = Me, H; R = $C_6H_4OC_nH_{2n+1}$; n = 1–6, 8, 10, 14
X = Me; R = C_mH_{2m+1}; m = 1–10

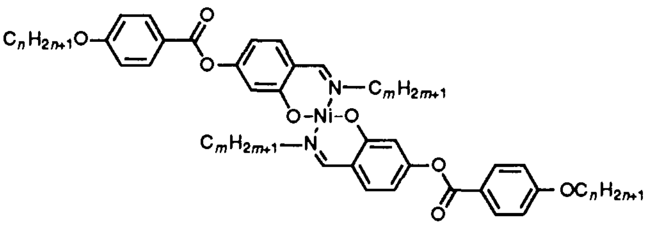


3: R = C_nH_{2n+1}; n = 5–10
R = OC_nH_{2n+1}; n = 4–8

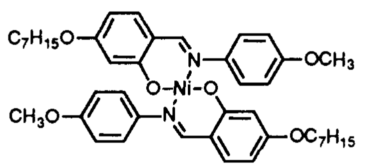
highly concentration dependent, indicating that some association was occurring; it was suggested that this might be taking place through intermolecular Ni···O—Ni association. Homologous nickel complexes **5**, investigated by Caruso et al.,[12] were found to exhibit nematic phases at higher temperatures than the corresponding copper salts. Ovchinnikov et al. have published an X-ray structure of a single crystal of complex **6**,[13] and X-ray studies in the nematic phase have been reported for complexes **7**.[14]



4: n = 4–12, 14, 16, 18



5: m = 1, n = 8, 11, 14
m = 13, n = 12



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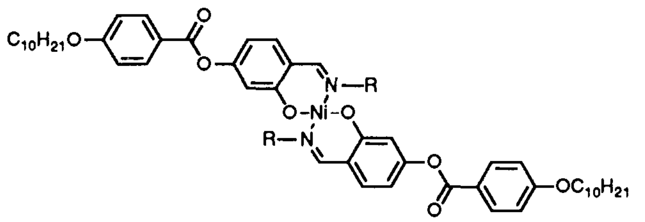


7: R = C_5H_{11}, $C_{10}H_{21}$, C_6H_4OMe

2. Dithiobenzoates

Detailed studies on the alkyloxy nickel dithiobenzoate complexes **8** have been reported by the Sheffield group[15] (n = 5–10) and by Ohta et al.[16] (n = 4 and 8); the phase diagram of the series synthesized by Bruce et al. is shown in Figure 4. No X-ray structural data are available, but the ^1H NMR spectrum (toluene-d_8 at 60 °C) of **8**, n = 8 shows it to be diamagnetic.[15a] The linear dichroism of the dithiobenzoates was measured by the Sheffield group[17] in the nematic solvent E7 (a mixture of *n*-alkylcyanobiphenyls and *n*-alkylcyanoterphenyls; Merck) and high order parameters (S_{op} = 0.7–0.8), for the nickel complex and its palladium analog were obtained. The purple-blue nickel complex dissolved in a nematic host can be used in a colored guest–host display device. A similar report has been made concerning the Giroud and Müller-Westerhoff nickel dithiolene complexes (**1**);[18] this indicates the potential for such complexes as dichroic dyes in displays.

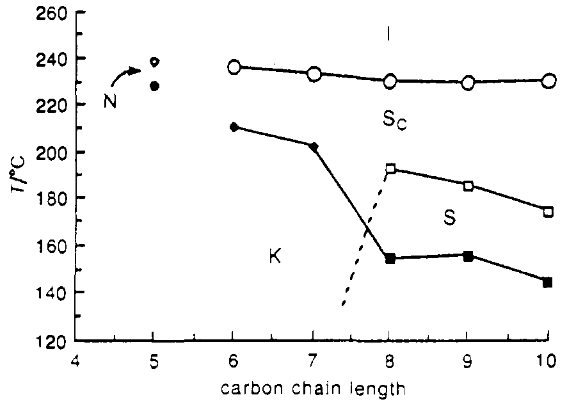
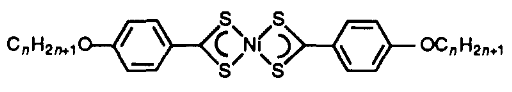


Figure 4. Phase diagram for nickel bis[4-(alkyloxy)dithiobenzoates] **8**. The symbols are as follows: ●, K–N; ◆, K–S_C; ◇, N–I; ■, K–S_X; □, S_X–S_C; ○, S_C–I.



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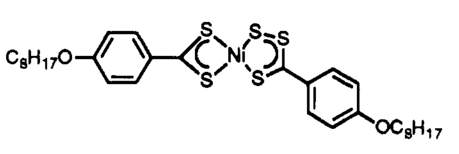
The strong color of the complexes has made phase characterization very difficult, but there seems general agreement that an S_C phase is present. Below this transition (at 155 °C) a highly viscous mesophase was observed for the n = 8 homolog, which was designated a S_H phase by Ohta's group. Both groups found the S_C phase on heating and then, above 230 °C, a color change from blue to red into the isotropic phase. The color change signaled a chemical reaction, and it was shown, by comparison with an authentic sample, that a mixed trithiobenzoate–dithiobenzoate complex (**9**) had been formed. The interconversions of bis-dithiobenzoate, bis-trithiobenzoate, and mixed di-/tri-thiobenzoate complexes have previously been explored for nonmesogenic complexes.[19]

The trithiobenzoate–dithiobenzoate complex **9** exhibited a nematic phase at 126 °C which cleared at 198 °C. Nematic behavior was also seen earlier (at 124 °C) in parts of the sample and double melting was proposed. While the n = 5 homolog of **8** showed a nematic phase, the n = 4 complex simply cleared from the blue solid into the red liquid but, on reheating, the "double melting" appeared and a nematic phase was exhibited.

To confirm the structural assignments, both the mixed complex **9** and the bis-trithiobenzoate complex **10** were synthesized; the transition temperatures found were (**9**) K–N, 126 °C; N–I, 198 °C; and (**10**) K–N, 133 °C; N–I, 161 °C and monotropic, (N–S_C) 95 °C.[15a] Both



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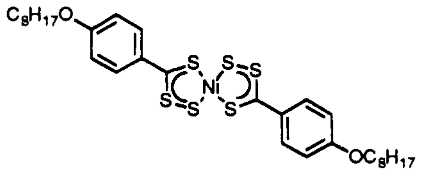
9 and **10** show significantly lower transition temperatures than **8**; this is likely to be due to the reduced anisotropy of the molecule, arising from a change from the linear **8** to a more bent form in **9** or **10**.



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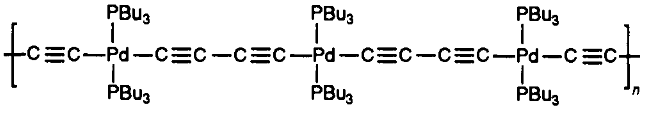
In addition to these nickel bis[(4-*n*-alkyloxy)-dithiobenzoates], Bruce et al.[20] have prepared a series of related complexes with 3-fluoro substituents in the benzene rings. All of them showed only S_C phases from $n = 4$ upward.

B. Palladium

Only metallomesogens of Pd(II) (d^8) are known; this configuration is again largely associated with square-planar geometry, although weak axial interactions (toward square-pyramidal geometries) are not uncommon. The first palladium complexes to exhibit liquid crystallinity were the very unusual polymers **11** and **12** reported by Takahashi et al.;[21] these were, however, lyotropic (in trichloroethylene solution) and were high melting and did not show thermotropic character. More recently this group has synthesized thermotropic platinum complexes of closely related types (section II.C).



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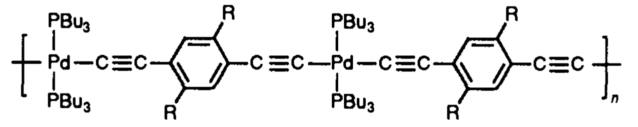


12: R = H, CH_3, C_2H_5

The Sheffield group has used a variety of ligands, including cyanobiphenyls and dithiobenzoates, for a systematic study of a wide group of metallomesogens, while Ghedini and his collaborators in Italy pioneered the mesomorphic orthopalladated azo complexes and related species, a topic which has recently been imaginatively developed by Espinet and his collaborators in Spain.

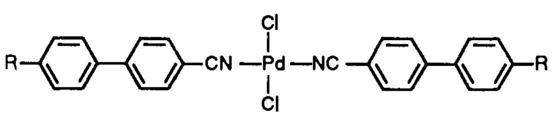
1. Cyanobiphenyls

The *trans*-dichloro complexes of *bis*(4-substituted-4′-cyanobiphenyls) **13**, bearing 4-*n*-alkyl chains have been synthesized. The shorter length 4-*n*-alkyloxy series only showed monotropic nematic behavior, but enantiotropic smectic phases were seen for longer chain length alkyloxy complexes.[22]

Table I. Birefringences of the Bis[4-(alkyloxy)-4′-cyanobiphenyl]palladium Complexes 13[a]

n	birefringence Δn
5	0.1608
6	0.1636
7	0.1473

[a] Measured by the rotating analyzer technique at a reduced temperature of 0.985.

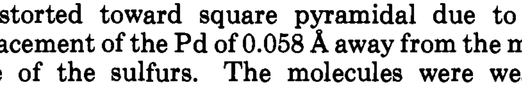


13: R = C_nH_{2n+1}, OC_nH_{2n+1}, $n = 1–12$

Measurements on these complexes, by Dunmur and his colleagues,[23] have compared the birefringence to that of the ligand in order to ascertain the effect, if any, of the metal on the birefringence (Table I). Increasing the length of the hydrocarbon tails on the mesogens normally also increases the polarizability anisotropy but decreases the number density, thus causing little overall change in the birefringence. In the case of the palladium complexes, however, the birefringence of the metallomesogen was higher than that of the corresponding 4-(alkyloxy)-4′-cyanobiphenyl ligand, indicating that the metal is playing a substantial role and enhances the birefringence.

2. Dithiobenzoates

Palladium dithiobenzoates **14**, analogous to the nickel complexes **8**, were also found to be mesomorphic by the Sheffield group.[15a,24] They were obtained as red powders for the shorter homologs ($n \leq 7$) and green powders for the longer chain length complexes. On heating, the green solids underwent a color change to red; similarly, on heating them in solution, the color changed and red crystals were isolated.



14: $n = 4–10$

A single-crystal X-ray structure of the red $n = 8$ homolog (Figure 5) showed the presence of monomeric palladium complexes containing the expected chelated 4-(octyloxy)dithiobenzoate ligands.[15a] The palladium showed approximate square-planar coordination, slightly distorted toward square pyramidal due to the displacement of the Pd of 0.058 Å away from the mean plane of the sulfurs. The molecules were weakly associated in pairs with intermolecular Pd···S distances of about 3.4 Å (cf. intramolecular Pd–S 2.29–2.35 Å). The structure of the green form is unknown, but it was suggested that it might be dimeric (cf. Figure 6) by analogy with the dimeric palladium dithioacetates of known structures.

The complexes showed S_C phases for $n \geq 4$, with those of chain length $n = 4–6$ also showing a nematic phase. Transition temperatures were fairly high with melting points generally above 200 °C and clearing points above 300 °C; the former were 20–30° and the latter ca. 80° higher than those of the nickel analogs. The complexes with $n = 8–10$ also showed a lower temperature crystal smectic phase which was not unambiguously identified

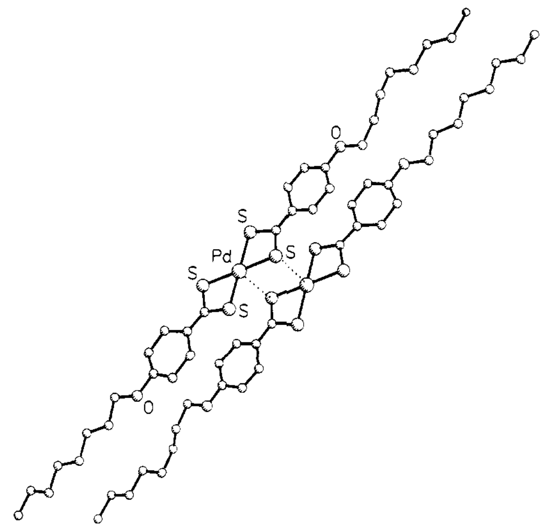


Figure 5. The single-crystal X-ray structure of palladium bis[4-(*n*-octyloxy)dithiobenzoate] (14) showing the intermolecular interactions.

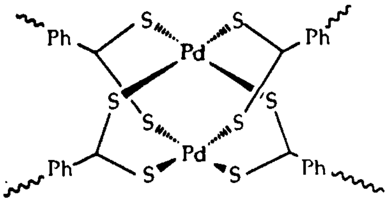
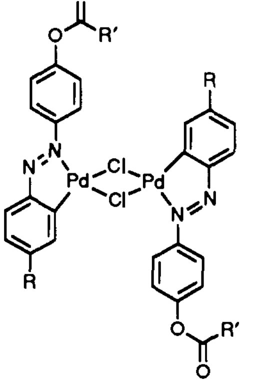


Figure 6. Representation of the possible structure of a dipalladium tetrakis[4-(alkoxy)dithiobenzoate].

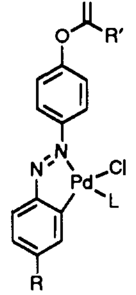
by X-ray, although optical observations were consistent with a crystal smectic G phase.[15a] EXAFS studies showed agreement with the X-ray data for the solid phases and also indicated no measurable axial interactions to be present in the S_C mesophase.[15b] Linear dichroism measurements of the $n = 6$–10 homologs in a nematic solvent showed[17] that these materials also possessed very high order parameters ($S_{op} = 0.86$), together with high contrast ratios (8.7–12.8).

3. Cyclopalladated Azobenzenes and Diarylazines

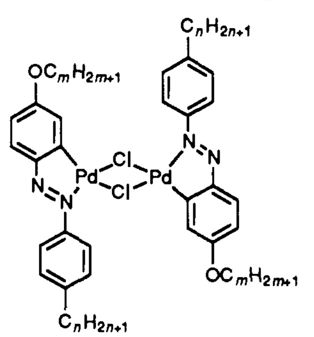
The dimeric metallomesogens **15**, based on cyclopalladated azobenzenes, which were first discovered by Ghedini et al.,[25] exhibited nematic phases at fairly high temperatures (~200 °C). Their mononuclear derivatives **16**, of reduced symmetry, formed smectic and nematic phases at lower temperatures.[26] Italian[27] and French[28] groups have carried out many studies on similar systems since then. More recently the cyclopalladated alkyl/alkyloxy azobenzene compounds **17** and **18** were synthesized,[29] by a route which reportedly gave a 1:1 mixture of the two isomers, except for $n = 1$, $m = 7$, which gave a single isomer, identified as **17**. The third (mixed) isomer (containing the left-hand side of **17** and the right-hand side of **18**) was apparently not seen. By comparison with the organic ligands, the cyclopalladated complexes showed more mesophases, but at much higher temperatures. The mesophase was actually induced by introduction of the palladium for $n = 1$, $m = 1$, while for the higher homologs the palladium stabilized the nematic phase enantiotropically. Thus, **17** ($n = 1$, $m = 7$) showed a nematic phase (175–194 °C) before clearing, whereas the uncomplexed ligand melted at 77 °C and only showed a monotropic nematic phase between 67 and 59 °C. It was also found that (a) the clearing points of the metallomesogens decreased to a larger extent with increasing chain length than those of the ligands, (b) the nematic phase ranges were larger in the metalated compounds, and (c) smectic behavior was seen for the $n = 1$, $m = 12$ complex.



15: R = EtO or Et; R^1 = C_4H_9, C_5H_{11}, C_6H_{13}, or $(CH_2)_8CH{=}CH_2$



16: L = pyridine, quinoline



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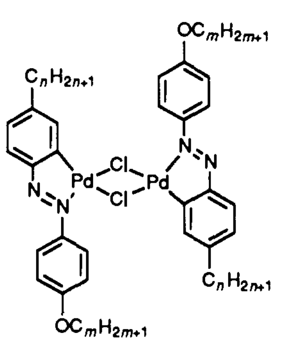

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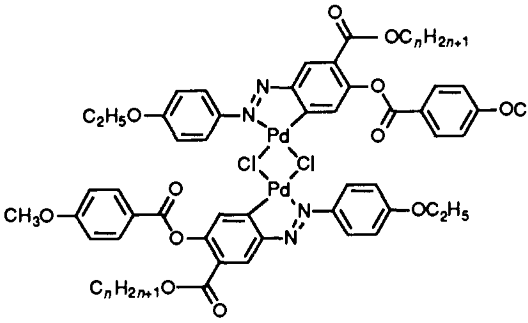
From qualitative interpretations of the calorimetric and optical data, and order parameters (measured using infrared spectroscopy), it was also suggested that the mesophases seen for the palladium complexes might possess biaxial ordering.

Hoshino et al.[30] in Japan have recently synthesized a new series of cyclopalladated complexes (**19**) based on the mesomorphic substituted azobenzene **20**, bearing a lateral ester chain. All the ligands and all the complexes showed single nematic phases, which oc-



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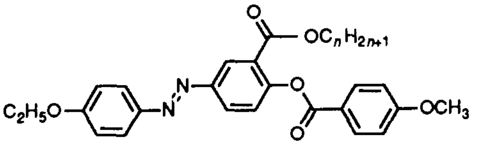

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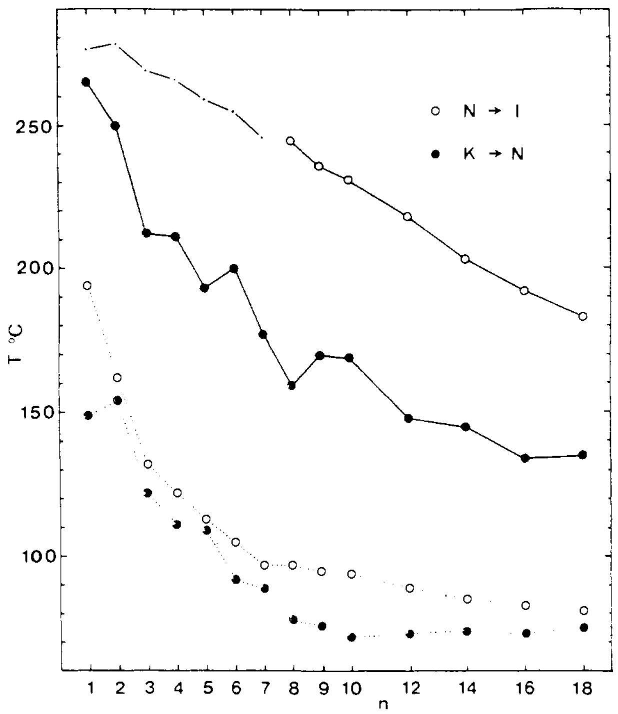


Figure 7. Phase diagram of the azobenzene ligands **20** (dotted lines), and their cyclopalladated complexes **19** (solid lines), showing the effect of increasing length of the lateral chain. (Reprinted from ref 30. Copyright 1991 Taylor & Francis.)

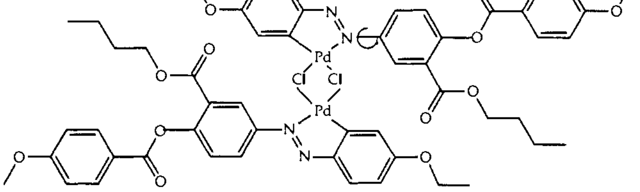
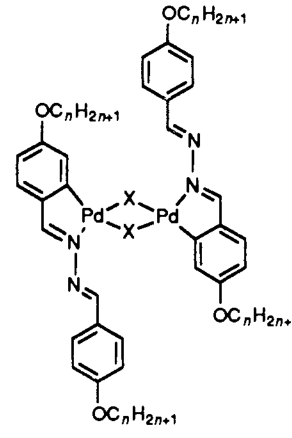


Figure 8. Schematic representation of the effect of rotation on the laterial substituent in the cyclopalladated azobenzene complexes **19**.

curred at higher temperatures and had broader phase ranges, for the complexes than for the corresponding ligands. The effect of the large lateral chains on the shape of the phase diagram (Figure 7) was discussed. For conventional organic systems, the lengthening of the alkyl side chains decreases the clearing temperature (T_{NI}) in a smooth curve until a limiting value is reached where T_{NI} is almost constant.[31] The reason for this is that short chain lateral substituents cause broadening of the molecule, leading to a decrease in T_{NI}, but on further lengthening the chain aligns with the molecule. There is then no further broadening and the T_{NI} curve levels out. The smoothness of the curve is explained by the lack of an odd–even effect due to the position of the chain in the molecule (i.e. in the core and not on the outer edges). ^1H NMR studies in solution suggested that in the nematic phase the molecules may undergo rotation about the N–C bond (Figure 8) thus causing the lateral chains to occupy the space in the molecular clefts formed by the three rigid rings and the Pd_2Cl_2 unit.[30] This would make the molecules more compact and explain the enhanced stability of the nematic phase.

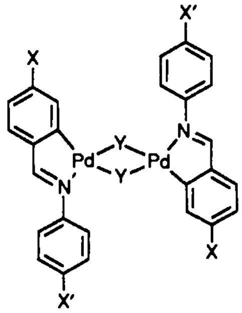
The Spanish groups have also developed cyclopalladated mesogens.[32] An important step in demonstrating the possibilities of unusual molecular shapes in metallomesogens was the synthesis of the orthopalladated azines, e.g., **21**,[33] as earlier reviewed.[1] These gave "book-shaped" molecules, due to the dihedral fold induced by the two bridging acetates, but which nevertheless showed mesomorphism (smectic C and, in one case, nematic phases). The effects of variation of the bridging group X on the phase behavior have been compared for the series **21b**. Introduction of a chiral bridging group, **21c**, gave a ferroelectric chiral S_C* mesomorph.[33] This showed electrooptic switching behavior and was the first ferroelectric metallomesogen.



21a: X = O_2CMe (n = 6–10, 12, 14)
b: X = Cl, Br, SCN, O_2CMe (n = 10)
c: X = $O_2C\overset{*}{C}HClMe$ (n = 10)

4. Cyclopalladated Arylimines

Ros et al. have recently published a study on the effects of polar end group position on the phase behavior of the orthopalladated arylimine systems **22**.[34] Some correlations between the type of substituent and the phase behavior was found in the uncomplexed ligands; for example chloro groups (X) favored S_A and S_B phases, methoxy end groups favored nematic phases, nitro and cyano encouraged S_A and nematic behavior, while the unsubstituted ligand showed no mesophases at all. The most desirable combination of properties, such as low melting points, enantiotropic phases, and broader phase ranges, were seen for the complexes bearing ligands with the most electron-withdrawing substituents (e.g. CN and NO_2), although the lowest melting points were obtained for the alkyl- rather than alkyloxy-substituted ligands.



22a: Y = CH_3COO, X = H, Me, OMe, Cl, CN, NO_2, X' = OC_8H_{17}
b: Y = CH_3COO, X' = H, Me, OMe, Cl, CN, NO_2, X = O_8H_{17}
c: Y = Cl, X = H, Me, OMe, Cl, CN, NO_2, X' = OC_8H_{17}
d: Y = Cl, X' = H, Me, OMe, Cl, CN, NO_2, X = OC_8H_{17}
e: Y = Cl, X = H, Me, OMe, Cl, CN, NO_2, X' = OC_6H_{17}
f: Y = Cl, X = H, OC_2H_5, OC_6H_{13}, $OC_{10}H_{21}$, X' = $OC_{10}H_{21}$

Table II. Phase Behavior of the Dinuclear Cyclopalladated Imine Complexes 22 and Their Mononuclear β-Diketonate Derivatives 23

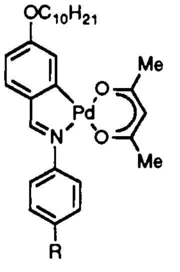
	transition temperatures, °C	
R or X′	dimer **22f**	monomer **23**
H	K 186 I (I 178 S_A)[a]	K-I
OC_2H_5	K 172 S_A 274 I	K 99, 109[b] N 118 I
OC_6H_{13}	K 146 S_A 268 I (S_A 140 S_C)[a]	K 84 S_A 118.5 N 125 I
$OC_{10}H_{21}$	K 133 S_C 204 S_A 243 I	K 74 S_A 128 I

[a] Monotropic. [b] Double melting behavior.

Espinet and co-workers found that the acetato-bridged palladium complexes **22a** and **22b** exhibited no mesophases; this was first thought to be because of the disruption of the planarity of the system by the acetato bridge which caused the molecule to fold. The bridging chloro group seems to encourage S_A behavior in the series **22c–e**, and a S_A phase is seen for all the compounds except those with a CN end group (which are nematogenic) and those with an H end group which are nonmesomorphic.

The effect of the terminal substituents on melting point differed slightly for **22c** (Me < Cl < OMe < NO_2 < H < CN) and **22d** (Me < Cl < OMe < H < CN < NO_2) and were very different from the order seen for the acetato-bridged complexes, **22a** and **22b** (H < CN < OMe < NO_2 < Me < Cl). Unlike the pattern found for the free ligands, no clear correlations between terminal substituents and phase behavior, or melting temperatures, could be found for the complexes. That indicated that core–core interactions were controlling phase behavior. Transition temperatures in the complexes were again raised considerably by comparison with the free ligands, and decomposition occurred on clearing to the isotropic for all the complexes.

In order to counteract the high transition temperatures, the Spanish workers have synthesized some mononuclear palladium complexes where the bridging ligands are replaced by acetylacetonate to give what has been termed a "P-shaped" molecule, **23**.[35] By comparison with the binuclear parent complexes, melting points were reduced by about 50 °C and clearing points by 120–150 °C. The disruption of the symmetry also encouraged the appearance of nematic as opposed to smectic phases (Table II).



23: R = H, OEt, OC_6H_{13}, $OC_{10}H_{21}$

A single-crystal X-ray structure determination of compound **24**, which shows a S_A and a nematic phase, has been reported (Figure 9).[36] This showed the Pd atoms to be in a square-planar array as part of a five-membered ring. The dimer molecule was not planar and had a Cl···Cl hinged dihedral angle of 141.3°, giving rise to a bent structure, with a Pd···Pd distance of 3.326 Å. The molecules in the unit cell exist in pairs (shortest Pd···Pd distance = 10.3 Å), and the crystal packing (Figure 10) was characterized by two-dimensional arrays of pairs of columns; the shortest Pd···Pd distance between columns was 7.038 Å and the shortest distance within a column was 6.485 Å. This result makes it clear that a dihedral angle in the molecule is not, by itself, sufficient to disrupt mesomorphism.

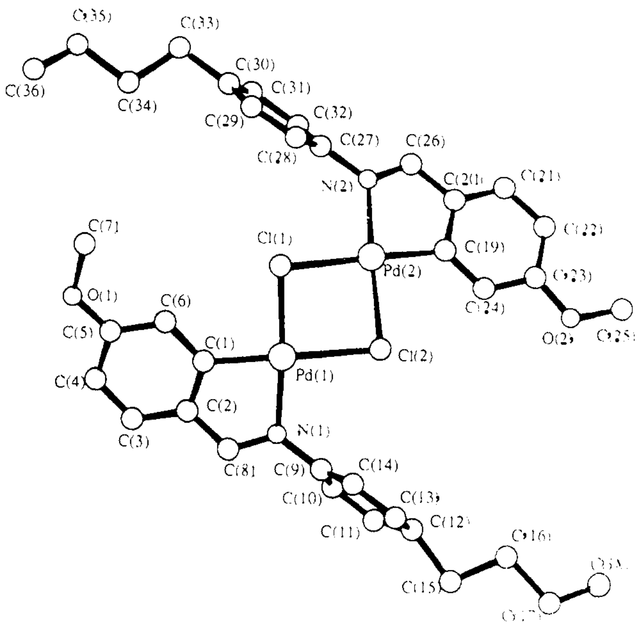
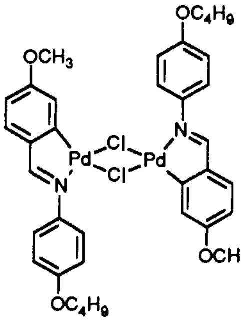


Figure 9. Single-crystal X-ray structure of the mesogenic cyclopalladated complex **24**. (Reprinted from ref 36. Copyright 1990 Taylor & Francis.)



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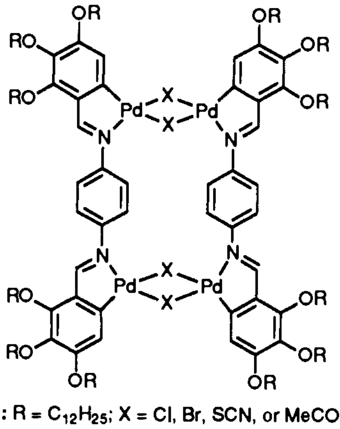
Praefcke et al.[37] have made the related tetrapalladium dimeric complexes **25** (R = $C_{12}H_{25}$; X = Cl, Br, SCN),



25: R = $C_{12}H_{25}$; X = Cl, Br, SCN, or $MeCO_2$

based on the diimine from *p*-phenylenediamine and 2,3,4-trialkoxybenzaldehyde. These complexes also exhibit enantiotropic mesophases, however, they are

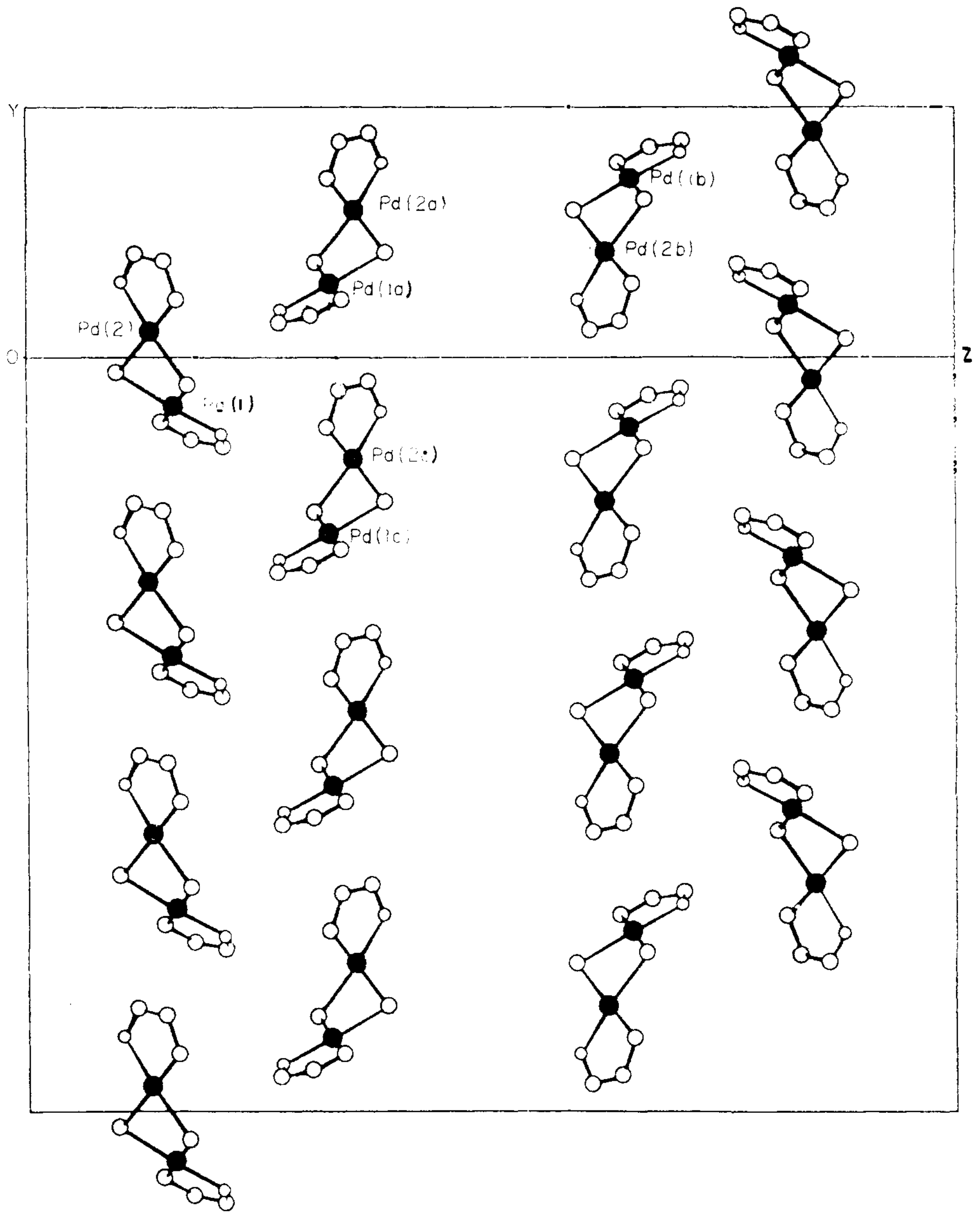
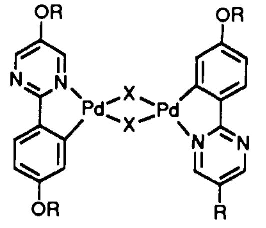


Figure 10. Schematic representation of the unit cell of the mesogenic cyclopalladated complex **24**, showing the dihedral angle at Cl···Cl. (Reprinted from ref 36. Copyright 1990 Taylor & Francis.)

discotic (D_h), in contrast to all the other orthopalladated complexes which are calamitic. This suggests that such complexes are close to the calamitic/discotic crossover point, where the mesophases will show behavior with some characteristics of each phase type.

5. Cyclopalladated Phenylpyrimidines

Ghedini et al.[38] have synthesized the dimeric cyclopalladated complexes **26**, based on the phenylpyrimidine ligand **27**. A single-crystal X-ray structure determination of **26** (R = C_6H_{13}, R′ = Me, and X = OAc) showed that the molecule was folded about the OAc group; neither this complex nor any other of the acetates were mesomorphic. The μ-halo complexes showed melting and clearing points at considerably higher temperatures than the ligands (Table III) and, while the ligands showed exclusively nematic phases, the palladium dimers showed only monotropic S_A phases (the monotropic phase transition temperatures are shown in brackets).



26: R = C_6H_{13}; R′ = CH_3, $C_{11}H_{23}$
R = C_9H_{19}; R′ = CH_3, C_9H_{19}
R = Cl, Br, I, OAc

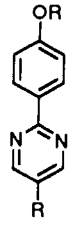


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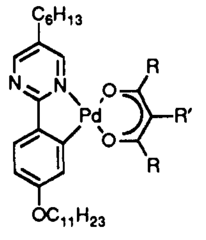
Table III. Phase Behavior of the Cyclopalladated Phenylpyrimidine Complexes 26[a]

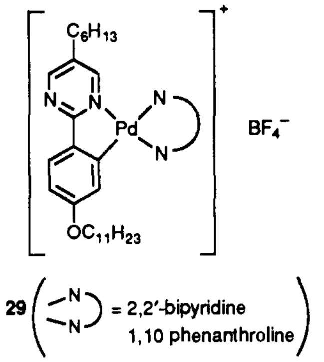
R	R′	ligand	X	complexes
C_6H_{13}	$C_{11}H_{23}$	K 48 N 59 I	Cl	(I 219 S_A 100 K)
C_6H_{13}	$C_{11}H_{23}$		Br	(I 202 S_A 171 K)
C_6H_{13}	$C_{11}H_{23}$		I	(I 193 S_A 149 K)
C_9H_{19}	CH_3	(I 38 N 32.5 K)	Cl	(I 168 S_X 137 S_A 129 K)
C_9H_{19}	CH_3		Br	(I 174.5 S_A 130 K)
C_9H_{19}	C_9H_{19}	(I 72 N 34 K)	Br	(I 197 S_A 106 K)
C_9H_{19}	C_9H_{19}		I	(I 202.5 S_X 128 S_A 105 K)

[a] Transition temperatures are in °C.

Mononuclear cyclopalladated complexes of the same ligand **27** have also been made[39] and the acetylacetonate **28** (R = Me, R′ = H) was found to exhibit a monotropic S_A phase, with a relatively low clearing point. The tetrafluoroborate complex **29** is a new example of an ionic calamitic metallomesogen, based on the phenylpyrimidine ligand, which shows an enantiotropic nematic phase at 146 °C and clears at 158 °C. Other salts, with the anions PF_6^- or SbF_6^-, or bearing chelate phenanthroline or dimethyl-substituted phenanthrolines, showed no mesomorphism.



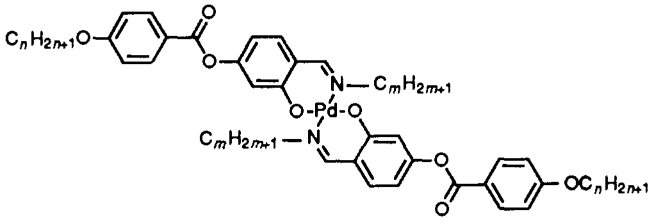
28: $R = CH_3$, $R' = H$
$R = C(CH_3)_2$, $R' = H$
$R = CH_3$, $R' = C_2H_5$
$R = CF_3$, $R' = H$



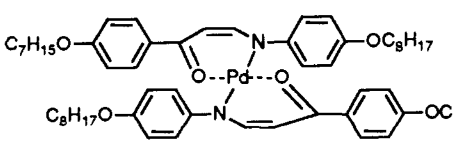
6. Salicylaldimines

Salicylaldimine palladium complexes **30** also show nematic phases, but at higher temperatures than their copper analogs.[12] It has been proposed that this may be due to the palladium only having a square-planar geometry, whereas the copper complexes could exist as mixtures of different configurations, thus leading to lower transition temperatures.

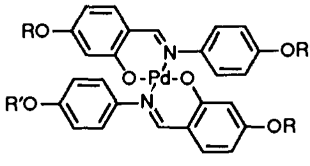
Smectic behavior has been found for the complexes **31** and **32** by the Russian group.[40] An X-ray crystal structure of the related mesomorphic complex **33** has been reported by Polishchuck et al.[41]



30: $n = 8-11, 14$, $m = 1$; $n = 7$, $m = 13$; $n = 8, 13$, $m = 8, 13$; $n = 14$, $m = 3$



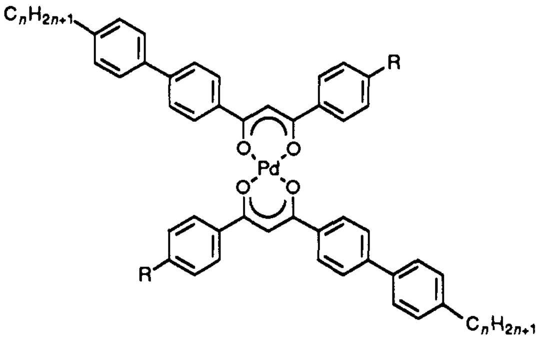
31: (K 232 °C S_A 272 °C I)



32: $R = C_7H_{15}$; $R' = C_8H_{17}$
33: $R = CH_3$; $R' = C_7H_{15}$

7. β-Diketonates

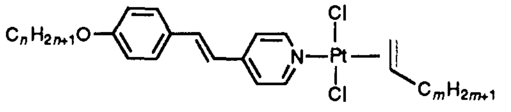
Sadashiva et al.[42] have made a series of β-diketonate palladium complexes **34** which, for $n = 12$, show monotropic nematic phases, when R = alkyl or alkyloxy, and S_A phases, when R = Cl, Br, or CN. This is similar to the behavior of related copper complexes (section III.A).



34: $n = 12$, R = Cl, Br, CN, Me, Et, OMe, OEt; $n = 5-12$, R = H

C. Platinum

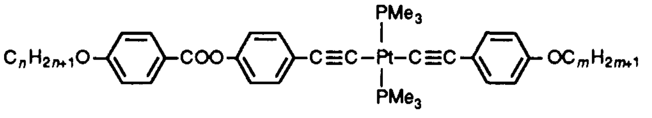
The only mesomorphic complexes are those of square-planar platinum(II). The platinum analogs of the cyanobiphenyl complexes **13**, and the bis(*n*-alkyloxy)-stilbazole complexes, $PtCl_2(n\text{-}OST)_2$, were extremely high melting ($n\text{-}OST = C_nH_{2n+1}OC_6H_4CH{=}CHC_5H_4N$). For this reason the noncentrosymmetric (*n*-alkyloxy)-stilbazole–olefin complexes **35**, $PtCl_2(n\text{-}OST)(CH_2{=}CHC_mH_{2m+1})$, were made by the Sheffield group,[43] with the expectation that, since less symmetric compounds pack less easily, they will melt at lower temperatures. The expectation was in fact realized, and some of the resultant complexes are currently among the lowest melting metallomesogens. Those complexes with $m + n$ = ca. 8–13 showed monotropic S_A character, while those with $m + n >$ ca. 13 showed enantiotropic S_A character. Increases of *n* and *m* have the twin effects of decreasing the stability of the crystal phase (lowering the melting point) and of increasing the clearing temperature, thus increasing the range of smectic phase stability. This observation is not surprising; smectic phases are promoted by increasing alkyl chain lengths, but since long hydrocarbon chains often increase the disorder in the crystal, they also cause the lowering of the melting point. These effects begin to plateau out with combined chain lengths $n + m$ of around 14 units. All the complexes **35** had transition temperatures below 100 °C, and the melting points could be lowered further, for example, to show a crystal to S_A melting transition at 45 °C, by mixing **35**, $n = 12$ and $m = 3$ with **35**, $n = 12$ and $m = 6$, in a 70:30 ratio. The mixing had little effect on the S_A to isotropic clearing temperature, and thus a substantially enhanced mesophase region was achieved in this way.



35: $m = 0-8$, $n = 3-12$

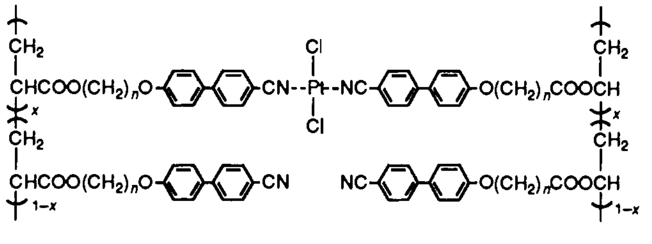
Other olefins were incorporated to give analogs of **35**, $[PtCl_2(C_{12}H_{25}OC_6H_4CH{=}CHC_5H_4N)(ol)]$. Of those investigated, only $[PtCl_2(C_{12}H_{25}OC_6H_4CH{=}CHC_5H_4N)(CH_2{=}CHCMe_3)]$ (K 95 °C S_A dec 110 °C) and the allyl ethyl ether complex $[PtCl_2(C_{12}H_{25}OC_6H_4CH{=}CHC_5H_4N)(CH_2{=}CHCH_2OEt)]$ (K 83 °C S_A 104 °C I) showed enantiotropic behavior.[43] Coordination of the internal alkenes, methyl oleate, and methyl elaidate, reduced efficient packing in the crystal, even further and thus the products were isotropic liquids, even at ambient.

Takahashi and his collaborators have recently reported the bis-alkynyl platinum complexes 36, related to the alkynylpalladium complexes 11 and 12.[44] However, by contrast to the lyotropic palladium complexes, 36 are thermotropic and show S_A (at ca. 175°), as well as nematic phases for longer tails (m, n = 12). When the [(n-alkyloxy)phenyl]ethynyl ligand in 36 was replaced by 1-octynyl, the complexes were not liquid crystalline, indicating that all the three benzene rings were needed for mesomorphism.



36: n = 5, 8, 10, 12, m = 8
n = 12, m = 5, 10, 11, 12

Polymers containing side-chain cyanobiphenyls bearing $PtCl_2$, 37, have been synthesized by Hanabusa et al.[45] Nematic phases were observed at low concentrations of metal coordinating to the cyanobiphenyloxy mesogen (<24 mol %); at higher concentrations, smectic behavior was seen, and then, at still higher concentration, mesomorphism was lost. This probably arose because of excessive cross linking through coordination to the Pt(II) centers.



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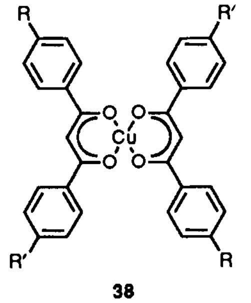
III. Group 11: Copper, Silver, Gold

A. Copper

Copper-containing metallomesogens form one of the largest areas of work in the field; all those exhibiting liquid crystalline character are of Cu(II) with an essentially square planar arrangement of ligand atoms about the metal. Many of the first ones reported were found to exhibit discotic phases (see ref 1). However, many calamitic copper mesogens have also been made, and these complexes provide some interesting metallomesogen chemistry and physics, in particular arising from the paramagnetism induced by the presence of the copper(II) (d^9) center, which can offer useful potential applications.

1. Substituted β-diketonates

Early work showed that the copper β-diketonates 38 (R, R′ = $C_nH_{2n+1}O$ or C_nH_{2n+1}), and 39, were discotic.[46] However Chandrasekhar et al.[47] found that the complexes 40 (n = 10; R = Me, Et, OMe, OEt, OPr), bearing a 4-substituted phenyl and a 4-substituted-4′-biphenyl on each diketone, were monotropic nematic and showed features of both rod- and disklike molecules; this was confirmed by Sadashiva et al.[42] who observed a monotropic S_A phase for 40 (n = 10, R = CN and Br). Mühlberger and Haase found that the cyclohexylphenyl complexes 41 (R = alkyl) were also nematic monotropic.[48]



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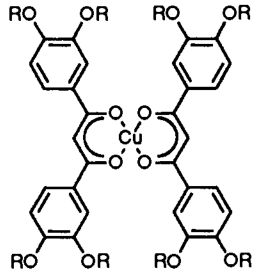

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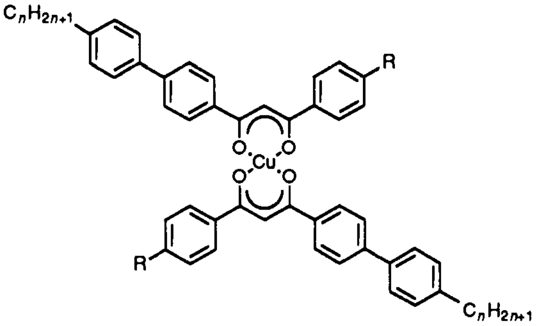

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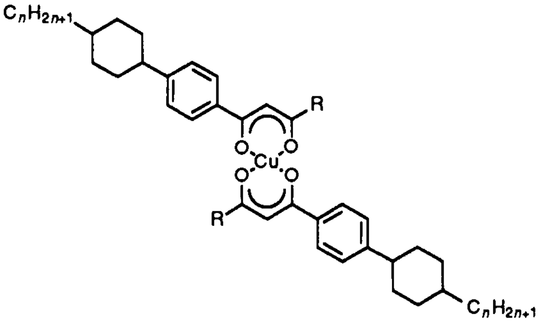

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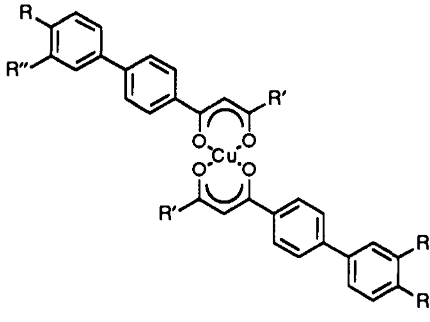
Gray, Goodby, and their collaborators at Hull have reexamined the problem and, while confirming the general conclusions of the Indian group, have pointed out that the complexes tend to decompose at the temperatures at which the isotropic phase is reached.[49] This brings some doubt to the accuracy of the transition temperatures, since monotropic phases are achieved by cooling, usually from the isotropic liquid. In order to attempt to lower melting points, and to define more precisely the borderline between discotic and calamitic behavior for such molecules, the Hull group has modified the design, by varying the length to breadth ratio, making the molecules either more rodlike or more disklike. They found that, while 42, (R = $C_{10}H_{21}$, R′ = Me, R″ = H) is not mesomorphic, 42 (R = $C_8H_{17}O$, R′ = Me, and R″ = F) and 41 (R = Me, n = 7) show monotropic nematic phases and the biphenyl cyclohexylphenyl complex 41 (R = 4-$MeOC_6H_4C_6H_4$, n = 7) and the three bis biphenyl complexes 43a (R = $C_{10}H_{21}$; R′ = Me, Et, or F) all showed enantiotropic N phases, identified by miscibility studies with the organic nematic 5-CT. In addition, the fluorobiphenyl complex, 43a (R = $C_{10}H_{21}$; R′ = F) showed an enantiotropic smectic A phase. It was empirically observed that nematic phase stability tended to increase with in-



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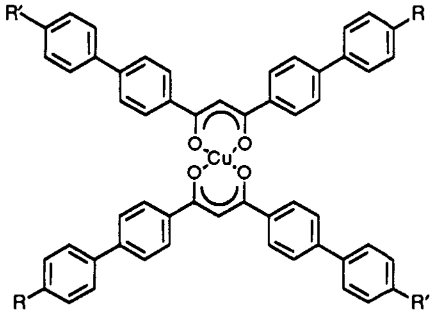
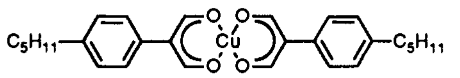


43a

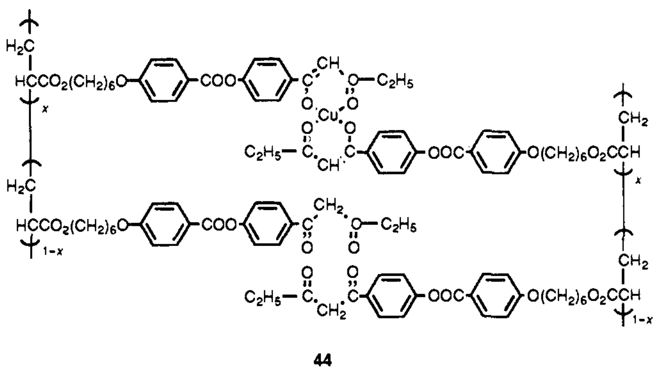


43b

creasing size of the so-called "lateral substituent" in these complexes. This is contrary to the trends observed for conventional rodlike organic liquid crystals where molecular broadening tends to depress phase stability. It was therefore proposed that these materials were not behaving as "rodlike" molecules, nor were they displaying discotic phases. Instead it was suggested that such molecules should be seen as an intermediate "elliptical stage" between the two extremes of rod- and disklike molecules.

Blake et al. have found that the complex Cu(RC-$(CHO)_2)_2$, **43b** (R = 4-$C_5H_{11}C_6H_4$), derived from the appropriate 2-substituted malondialdehyde, shows a high-temperature enantiotropic nematic phase (K-(220 °C) → N-(230 °C) → I).[50] Neither the corresponding 3-aryl-2,4-pentanedionato complex $Cu(RC(CMeO)_2)_2$ nor $Cu(C_5H_{11}C(CHO)_2)_2$ was mesomorphic.

Hanabusa et al.[51] have reported the copper-containing materials **44** and **45** to be mesomorphic; **44** is based on an acrylate polymer where each acrylate ester bears a side chain to which a β-diketone is attached. Increasing the percentage of copper units in the polymer **44** resulted in better monoaxial orientation in the nematic phase, with the plane of the (square-planar) copper complex aligning parallel to the fiber axis. The polymer **45**, based on dibenzoylmethane, where the phenyl rings are linked by $O(CH_2)_nO$ spacers, was reported to exhibit smectic phases.



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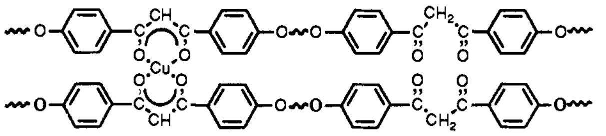
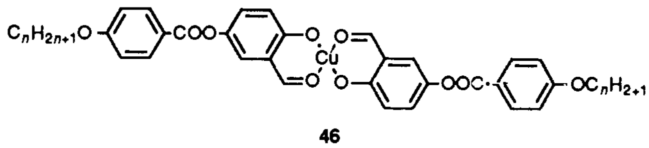


45

2. Salicylaldehydes

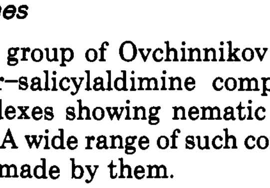
The complexes **46**[52] based on 2,5-dihydroxybenzaldehyde (where the 5-hydroxy is esterified by *p*-(alkyloxy)benzoate with *n* = 6–10, 12, and 14) showed a S_C phase for the $n \geq 8$ homologs and decomposed on clearing to the isotropic. ESR measurements carried out on **46** (*n* = 14) in the S_C phase at 240 °C showed that a paramagnetic contribution was made by the copper core and that the molecules began to align perpendicular to the magnetic field. On heating to 250 °C, the diamagnetic contributions of the aromatic rings began to dominate, and the perpendicular alignment was disturbed. This was accompanied by decomposition.



46

3. Salicylaldimines

The Russian group of Ovchinnikov made the first smectic copper–salicylaldimine compounds **47** and reported complexes showing nematic phases shortly thereafter.[53,54] A wide range of such complexes (Table IV) have been made by them.



47

A series of single-crystal X-ray, ESR,[66] IR and visible spectroscopy, calorimetry and optical microscopy studies were carried out on the complexes **47**. Results from these investigations[67] and comparison with similar systems containing other metals (zinc, cobalt, nickel, palladium, and vanadyl)[68] indicate the role of the metal in determining phase behavior. The different properties are governed by the geometrical structures of the molecules which, in turn, depend on the geometry of the coordination site. Thus, Cu and Pd complexes have planar or nearly planar arrangements around the metal and give rise to flat elongated molecules suitable for mesophase formation. In contrast, Zn, Co, and Ni complexes of this type have a tetrahedral coordination and do not show any mesomorphism.

The results of ESR measurements of the copper complexes (in dilute solutions, in the isotropic melt, in the crystal state, as well as in the mesophase) have led

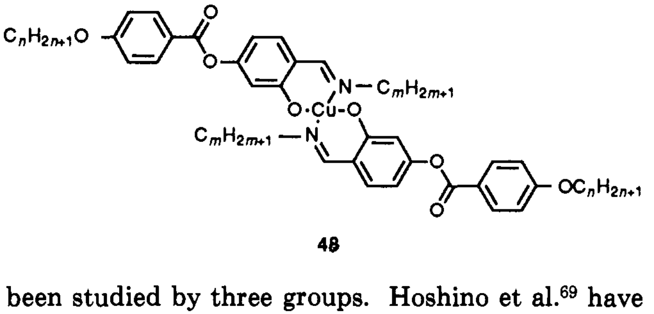
Table IV. Salicylaldimine–Copper Complexes 47 Synthesized by Ovchinnikov et al.

n = 1–12, R	m = 1–12, R′	phases
H	H, C_mH_{2m+1}	
	$C_6H_4OOCC_6H_4OC_mH_{2m+1}$	S_1, S_A[55]
$C_nH_{2n+1}OC_6H_4CO$	$C_6H_4OC_mH_{2m+1}$	S_A
OC_nH_{2n+1}	$C_6H_4OC_mH_{2m+1}$	
	$C_6H_4C_mH_{2m+1}$	S_1, S_C, S_A
	C_6H_4X (X = F, Cl, Br, NO, CN, NMe_2)	
OC_7H_{15}	m-FC_6H_4 p-FC_6H_4,[56] C_6F_5,[57] C_6H_5	S_A
	C_6H_4X, (X = CN,[58] OC_9H_{19},[59] NO_2,[60] OC_8H_{17},[61] OC_5H_{11},[62] OMe,[63] Me[64])	S_1, S_C, S_A
	$O_2CC_6H_4OC_{12}H_{25}$	
		N
OC_5H_{11}	$C_6H_4OC_mH_{2m+1}$[65]	S_1, S_C, S_A

to the following proposals. In dilute solutions all the complexes (including nonmesomorphs) have the same, almost planar, trans configuration. On increasing the concentration (i.e. in the isotropic melt), the mesomorphic molecules remain planar while the nonmesomorphs are distorted, thus losing the ability to form phases. On cooling to the mesophase, it is proposed that some of the initially planar molecules in the phase convert into a tetrahedrally distorted form, prior to the formation of a crystal lattice. As the temperature falls further, the distorted molecules agglomerate into individual isotropic, microscopic droplets while the rest of the planar molecules form the smectic phase, the overall effect being to give rise to a heterogeneous mesophase.

Evidence for this heterogeneous phase comes from an extrapolation from the solid state, where both tetrahedral and square planar isomers have been shown to be present by ESR and X-ray studies. Analysis of the single-crystal X-ray data showed that the crystal lattice was made up of alternating *trans*-square-planar and tetrahedrally distorted complexes, in parallel layers with the alkyl chains oriented perpendicular to the layers. X-ray studies have also suggested that smectic phases are formed in the melt, when the long axes of the copper complexes lie perpendicular to the layer planes in the solid state. If, on the other hand, the molecular long axes of the molecules lie in the plane of the layer, the layer order is lost on melting, and nematic phases are formed. The structure of the smectic phase has not been determined unambiguously, but is thought to contain the central, rigid parts of the molecules in a crystal lattice with "molten" alkyl chains forming a liquidlike domain between the layer planes.

The bis[4-[(4-alkoxybenzoyl)oxy]-*N*-*n*-alkylsalicylaldiminato]copper(II) complexes (**48**) have recently



48

been studied by three groups. Hoshino et al.[69] have investigated the complexes with m = 3, n = 4–12, 14, 16, 18, and m = 1, 2, 4–13, n = 6, Caruso et al.[12] the homologs with m = 1–15, 17, n = 10, 6, and m = 8, 13, n = 7–14, and Marcos et al.[8,9,70] those with m = 1, 5, 10, n = 10.

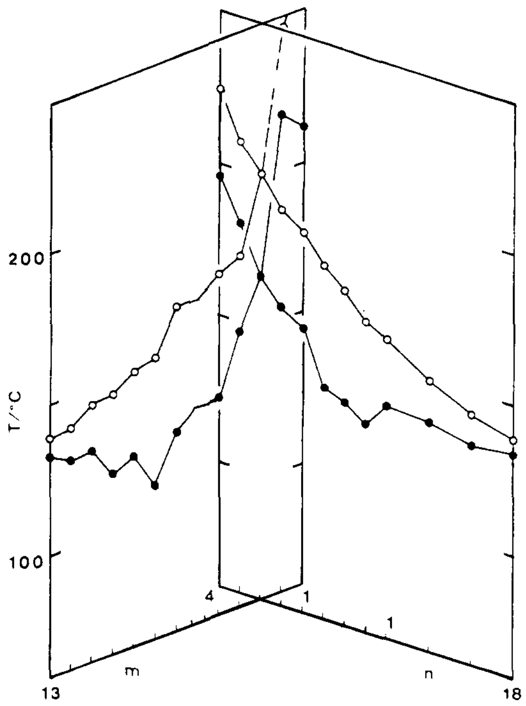


Figure 11. Phase diagram showing the effects of terminal (n) and lateral (m) alkyl chain lengths on the transition temperatures on the copper salicylaldiminato complexes **48**. (Reprinted from ref 69. Copyright 1990 American Chemical Society.)

Hoshino et al. found that all their compounds showed a single nematic phase and that elongation of the terminal chain (C_nH_{2n+1}) of the m = 3 series had the effect of bringing clearing temperatures down gradually. By contrast, initial increases in the length of the lateral chain (C_mH_{2m+1}) of the n = 6 series brought them down sharply, but the effect was reduced on further elongation (Figure 11).[69] For both series the melting points fell initially on elongation, up to a chain length ca. 8, after which they leveled out and even began to increase slightly.

Caruso and his collaborators obtained rather similar results but noted that in compounds with the same sum of (n + m) carbon atoms (e.g., n = 6, m = 13; cf, n = 14, m = 5), the transition temperatures were higher for those with longer lateral chains.[12] As well as the nematic phases seen for the shorter chain length homologs, S_C phases appeared for combinations of the longer chain length complexes ($n \geq 10$, $m \geq 11$) and for some combinations of long and short chain length substituents.

X-ray diffraction measurements of aligned monodomain samples of the materials in the mesophase, carried out by Marcos et al., showed that the complexes had negative magnetic susceptibility as they aligned perpendicular to the applied magnetic field.[8,9,70]

The anilino complexes **49** and those derived from methylamine, **50**, also described by the Spanish workers,[14] were found to have positive diamagnetic anisotropy and aligned parallel to the field. The difference between **48** and **49** was the increased diamagnetic contribution of the extra aromatic rings in **49**, which canceled out the paramagnetic effect of the copper core. It was suggested that the aromatic rings in **48** were

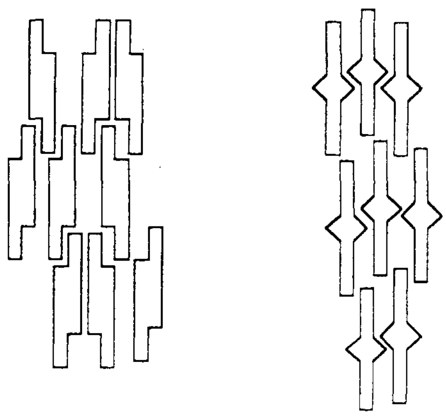
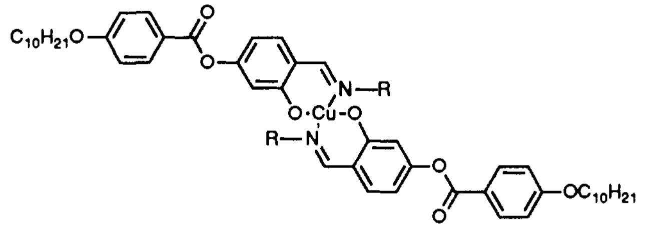
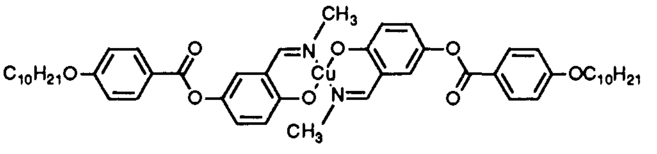


Figure 12. Schematic representation of the mesophase structure of the salicylaldiminato copper complexes 48 and 49: (left) complexes with long lateral substituents (parallel and interdigitated) and (right) complexes with short lateral substituents. (Reprinted from ref 14. Copyright 1991 Taylor & Francis.)

coaxial, unlike those in compound 49, and the diamagnetic contribution of the rings was therefore more efficient. X-ray data suggested that the complexes 49 with longer lateral chains interdigitated considerably in the mesophase while the complexes 48 ($m = 1$), with lateral methyls, existed in the fully stretched out "rodlike" manner (Figure 12).



49: R = C_6H_4OMe, $C_6H_4OC_{10}H_{21}$



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A further study on the effect of lateral substitution in the copper salicylaldimines 51 and 52 has been carried out by Bui et al.,[71,72] who compared (Table V) the phase behavior of the complexes 51 (and their nitro analogs) to that of the unsubstituted complexes. It was found that, as for conventional organic systems, the nematic phase range and stability decreased in proportion to the van der Waals' radius of the substituent. With the disubstituted complexes 52, the stability was reduced even further, giving rise to monotropic nematic phases. The phase stability was reduced to a greater extent when the larger substituent was in the 3-position due to the larger perturbation of the planarity around the copper core (Figure 13).

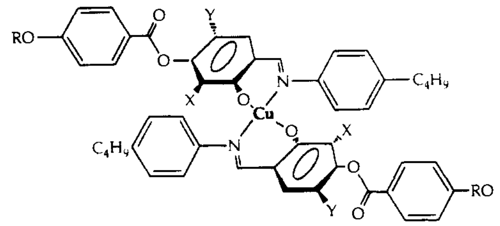
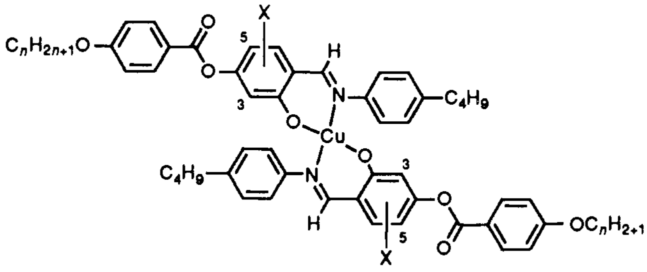
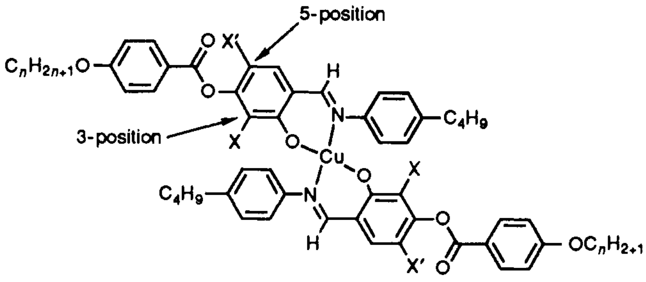


Figure 13. Schematic representation of the effect of a 3-lateral substituent on the planarity about the copper in complex **52**.

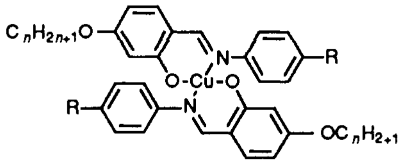


51: n = 2, 4, 6, 8, 10, 12, 14, 16; X = H, Cl, Br, I



52: n = 2, 4, 6, 8, 10, 12, 14, 16; X = Cl, X′ = Cl, Br; X = Br, X′ = Cl, Br

Ghedini and his collaborators have carried out X-ray diffraction,[73] EXAFS,[74] ESR,[75] and quasielectric neutron scattering (QANS)[76] measurements on the copper complexes 53. All show S_A phases, monotropic for the shorter and enantiotropic for the longer tail homologs; S_E and S_B phases were seen for the complex with $n = 12$, $m = 4$.



53: R = C_mH_{2m+1}, n = 1–4, m = 12; n = 12, m = 1–4, 6, 8; n = 4, = 7
R = OC_6H_{13}, n = 12

EXAFS studies can give information on the near neighbor interactions, distances, and geometries around the metal center in the mesophase. The EXAFS data on 53 ($n = 12$, $m = 4$) in the S_B phase were consistent with the presence of another Cu atom at 3.85 Å, two

Table V. Transition Temperatures (°C) of the Salicylaldiminato Copper Complexes 51

	substituent X (position)				
n	H	Cl (3)	Cl (5)	Br (3)	Br (5)
4	K 231 N 261 I	K 234 N 251 I	K 238 N 245 I	K 227 N 240 I	K 215 N 237 I
8	K 195 N 257 I	K 184 N 228 I	K 197 N 221 I	K 188 N 200 I	K 184 N 211 I
12	K 173 N 248 I	K 164 N 209 I	K 172 N 183 I	K 179 N 185 I	K 154 N 187 I
16	K 158 N 233 I	K 148 N 196 I	K 158 N 183 I	K 174 N 179 I	K 125 N 165 I

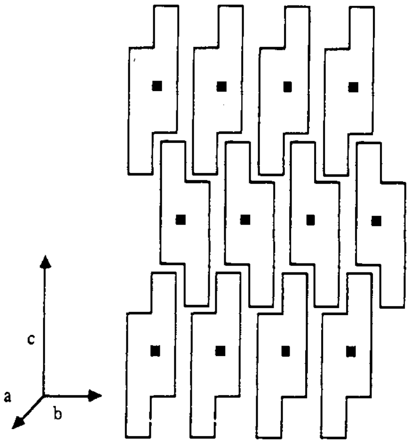
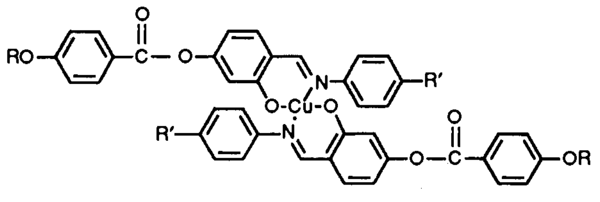


Figure 14. Schematic representation of the two-dimensional array [(100) plane] of interdigitated (salicylaldiminato)copper complexes **53** in the S_A phase. (Reprinted from ref 75. Copyright 1991 American Chemical Society.)

oxygens at 1.85 Å and two nitrogens at 2.0 Å from the central copper.[74] It was also concluded that the copper atoms possessed short-range correlations within the layers, and the ESR spectra reinforced the suggestion that the S_B phase was biaxial and had a higher degree of order than normal.[75] The X-ray diffraction experiments showed that the S_A phase existed in a two-dimensional array of interdigitated molecules with periodicities along the *b* and *c* axes of 8.6 and 30.22 Å respectively (Figure 14).[74]

The QANS experiments showed a translational diffusion coefficient smaller than those obtained for conventional organic liquid crystals.[76] Data for the S_A phase of **53** (n = 12 and m = 4) were interpreted in terms of the interdigitated aliphatic chains undergoing a hindered rotation, with the rigid cores remaining at rest. This is unlike models for S_A phases seen for organic materials, where free rotation of the molecules about their long axes is postulated.

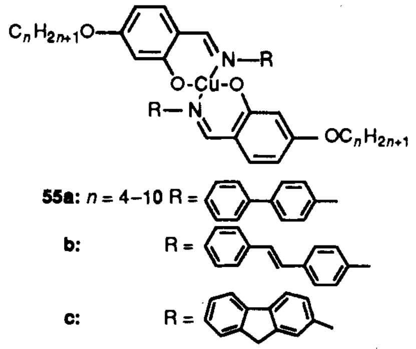
Haase et al.[77] have investigated the magnetic susceptibilities and X-ray diffraction patterns of compounds **54**. Order parameters of up to S_{op} = 0.575 and evidence for skewed cybotactic ordering in the nematic phase were obtained.

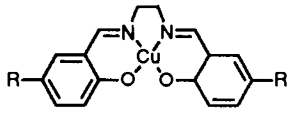


54: R = C_6H_{13}, R' = C_4H_9, OCH_3
R = C_4H_9, R' = C_4H_9, OCH_3

Three series of copper salicylaldimine complexes **55**, which differ in the nature of the substituent attached to the azomethine nitrogen, were synthesized by Reddy and Brown.[78] The complexes **55a** showed enantiotropic S_A phases for $n \geq 6$ and monotropic S_A phases for **55b** with $n \geq 6$. Series **55c** seemed to be fairly unstable so phase characterization was difficult, although from DSC and optical observations, it was thought that the n = 7 homolog also showed a S_A phase. Dilute solutions of the n = 7 homologs of all the complexes showed luminescence.

Paschke et al.[79] have reported the phase behavior of the [bis(5-alkylsalicylidene)ethylenediaminato]copper(II) complexes **56**, and have compared it to that shown by the alkyloxy analogs.[10] S_A phases were seen for all the complexes **56** with clearing temperatures at around 280 °C. Two phases below the S_A, observed by microscopy, may be S_H or S_G.



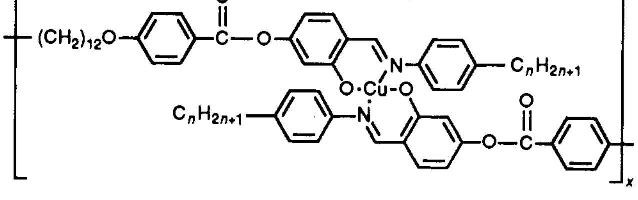


56: R = C_nH_{2n+1}, n = 5, 6, 8–10
R = OC_nH_{2n+1}, n = 4–8

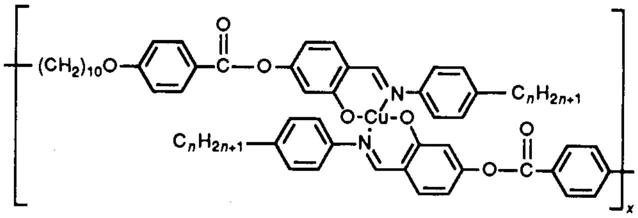
4. Salicylaldimine Polymers

In addition to the two examples of polymeric copper salicylaldimine mesogens[80] already reviewed, the phase characters of **57**[81] (with a 12-unit flexible spacer) and **58**[82,83] (with a 10-unit flexible spacer) have been examined. The former exhibit monotropic nematic behavior for n = 7–10, with clearing temperatures higher than those of the corresponding monomers and which decreased on increasing the length of the lateral chain.

Compounds **58** showed enantiotropic nematic phases for n = 5 and 10, and ESR measurements showed that there were two crystalline forms of the polymer, one of which contained the Cu in a square planar conformation.



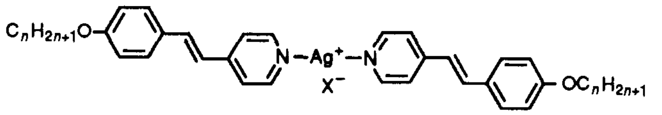
57: n = 4–13



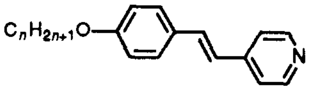
58: n = 1, 5, 10

B. Silver

The Sheffield group has carried out an extensive investigation of complexes of the type $[Ag(n\text{-}OST)_2]^+X^-$ (**59**), where n-OST is the stilbazole ligand (**60**).[84] The complexes with X = BF_4 were unstable to light and heat and formed smectic phases at high temperatures, whereas those with X = NO_3[85] showed S_A and S_C phases. With the larger CF_3SO_3 anion, a nematic phase was seen for the n = 1–4 homologs and thereafter S_A and



59: $n = 1–12$; X = NO_3, CF_3SO_3, BF_4, $C_{12}H_{25}OSO_3$(DOS), $C_8H_{17}OSO_3$(OS)



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S_C phases, together with a crystal smectic G phase, identified by microscopy. Conductivity measurements carried out in solution[86] on some of the CF_3SO_3 salts showed these materials to be very poor conductors and thus they may exist as tight ion pairs.

The single-crystal X-ray structure of the nematic methoxystilbazole–octyl sulfate complex, $[Ag(NC_5H_4\text{-}CH{=}CHC_6H_4OMe)_2]C_8H_{17}OSO_3$ (Figure 15),[87] showed the structure to consist of pairs of approximately linear (170.5°) bis-stilbazolesilver cations held together by pairs of octyl sulfates, the oxygens of which bridged the two silvers, approximately at right angles (∠N–Ag–O 88–93°) to the N–Ag–N axes. This completed an approximately square coordination about each metal atom. Two of the oxygens of each sulfate bind to the two silvers, one binds to the octyl, and the remaining oxygen binds to a bridging water. Hence the structure can be viewed as a quasipolymer held together by ionic Coulombic attraction and hydrogen bonds, $[\{\cdots(ROSO_3)\text{-}(AgL_2)_2(O_3SOR)\cdots HOH\cdots\}_n]$. It is tempting to speculate that this bonding network may assist the mesomorphism. Nematic phases are seen for methoxy- to (n-hexyloxy)stilbazole complexes; while the hexyloxy to dodecyloxy complexes showed S_C and S_A phases.

By comparison with the BF_4 salts, the use of the long-chain $C_8H_{17}OSO_3$ (octyl sulfate) and $C_{12}H_{25}OSO_3$ (dodecyl sulfate),[88] as counteranions (X) in **59** brought the melting and clearing temperatures down considerably; these salts showed a greater tendency to form nematic phases and a richer polymorphism was observed (Figure 16). This may be due to the broadening effect of the interdigitated alkyl chain of the anion which acts as a barrier by virtue of its position, thus reducing intermolecular side-to-side interactions between the aryls.

The dodecyl sulfate series also shows the appearance of a cubic phase reminiscent of the D phase. Cubic phases, which are viscous, optically isotropic mesophases, are uncommon and not yet well understood. For organic phasmidic materials, Levelut et al.[89] have proposed that the cubic phase may be more like the infinite periodic minimal surface (IPMS) model suggested for lyotropic cubics rather than the micellar model (Figure 17), and it is easier to imagine these ionic complexes fitting into this new model rather than into the crowded micellar system. The octyl sulfate salts show similar transition temperatures and phases to the dodecyl sulfate complexes, but the cubic phase is not seen.

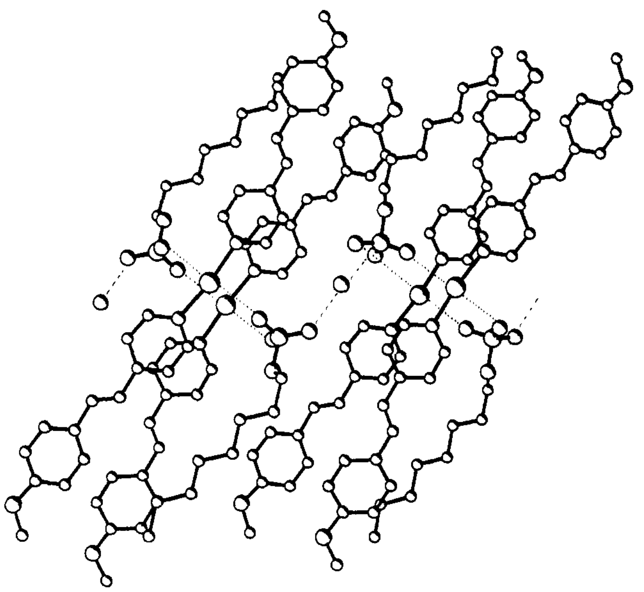


Figure 15. Single-crystal X-ray structure of the bis(4-methoxystilbazole)silver octyl sulfate complex.

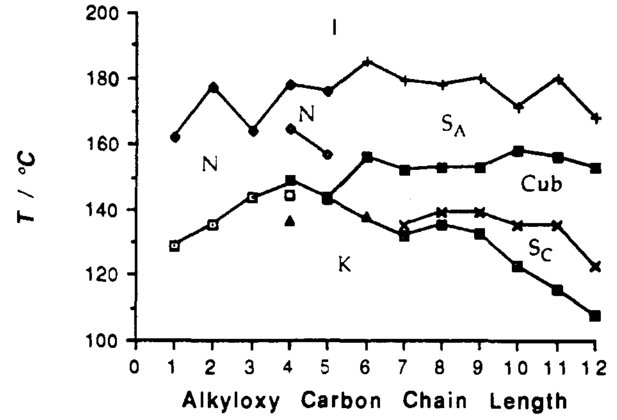


Figure 16. Polymorphism exhibited by the bis[4-(alkyloxy)syilbazole]silver dodecyl sulfates **59**. Symbols are as follows: ◘, K–N; ◆, N–I; ◘, K–S_A; ◇, S_A–N; ■, (S_A–S_C); □, (S_A–N_R); ▲, (N_R–S_C); ▲, K–Cub; □, Cub–S_A; +, S_A–I; ⊞, K–S_C; ×, S_C–Cub.

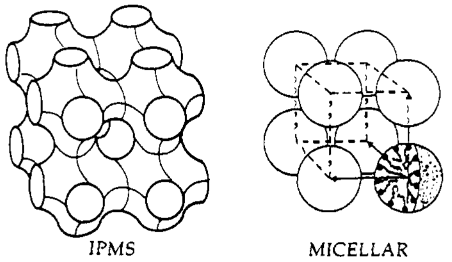
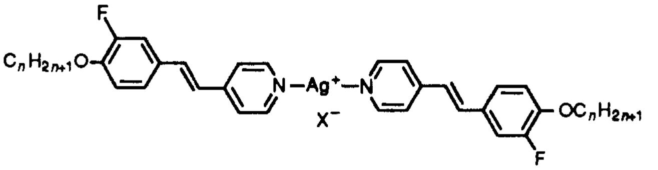


Figure 17. Diagrammatic representations of an infinite periodic minimal surface (IPMS, left) and of a micellar aggregate (right) (from ref 89).

Fluorinated stilbazole ligands,[90] and their complexes with silver salts, have been synthesized, and the effect of lateral fluorination on the phase behavior has been investigated.[91] It was found that clearing temperatures increased somewhat on fluorination in the 3-position in **61** while the melting points decreased (Figure 18), giving an overall increase in the range and the stability of the S_A phases. Nematic behavior was reduced and was only observed for the two shortest chain length members of the dodecyl sulfate series and the cubic phase was not seen. The effect of 3-fluorination was



61: $n = 1–12$; X = CF_3SO_3, DOS

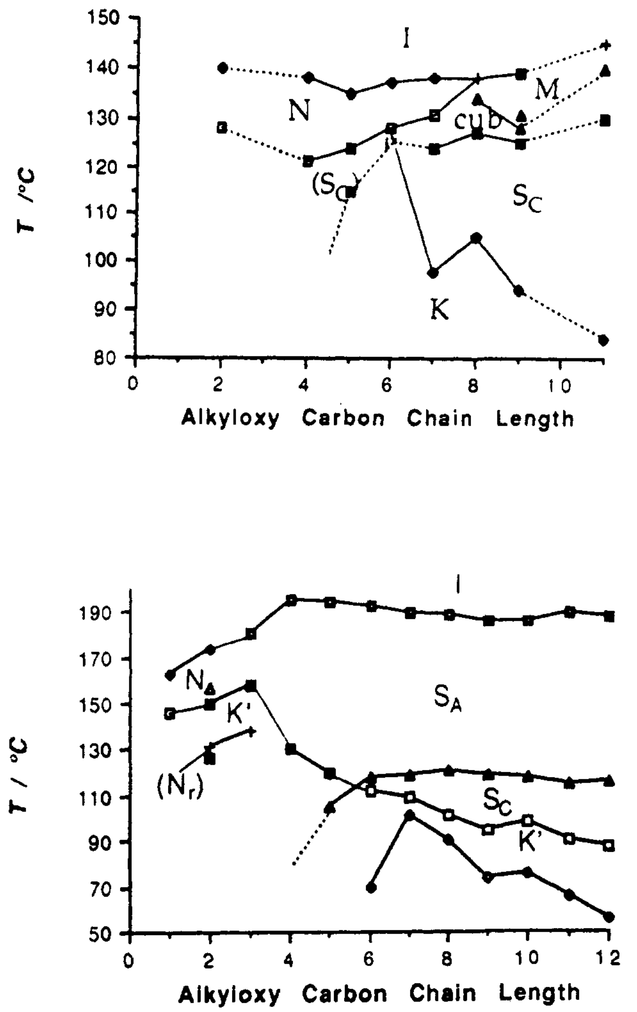
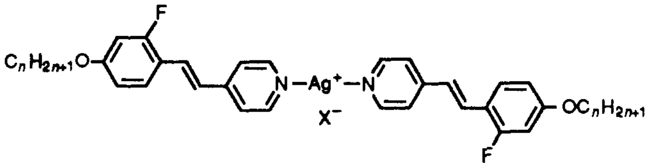


Figure 18. Phase diagrams of the effect of fluorination in the 2 (top) and the 3 (bottom) positions on the transition temperatures in the (fluorostilbazole)silver complexes 62 and 61. The symbols are as follows: (top) ⊡, K–N; ●, N–I; ◘, (N–S_C); ◇, K–S_C; ■··, S_C–cub; □, K–N; ▲··, Cub–M; ▲–, M–cub^r; ■–, cub^r–I; +, M–I; and (bottom) ⊡, K–N; ◆, N–I; ◘, S_A–I; ◇, K–K′; ■, K′–S_A; □, K′–S_C; ▲, S_C–S_A; △, S_A–N; ■, (S_A–N_r); +, K–K′; ■, K–S_A.

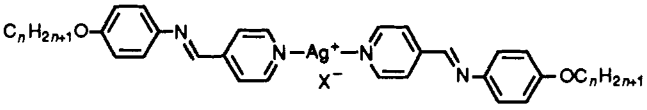
similar to that seen in conventional liquid crystals and corresponded to the "outer edge" effect discussed by Thompson et al.[49] for the terphenyl systems. It probably occurs because of increased lateral interactions between molecules bearing the 3-fluorophenyl substituent on the ligand.

The reverse effect was seen in the 2-fluorinated series 62, which showed a lowering of clearing points compared to the non-fluorinated materials, reduced smectic and enhanced nematic behavior.[91] This is typical and due to the broadening effect of the fluorine which increases intermolecular distances and dilutes intermolecular interactions. In one case (n = 7, X = dodecyl sulfate) a cubic phase is seen between a S_C and a nematic phase.

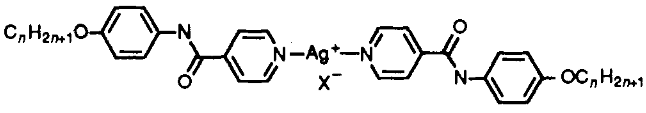


62: n = 2, 4–9, 11; X = CF_3SO_3, DOS

The salt $[Ag(n\text{-OIP})_2]^+X^-$ (63, n = 2 and X = BF_4, where n-OIP is the 4-[[4-(alkyloxy)phenyl]amino]-pyridine ligand), made by the Zaragoza group, showed a nematic phase. Others in the series and 64 showed S_A or S_C phases.[92] The salts $[Ag(n\text{-OCP})_2]^+X^-$ (64) carrying the (alkyloxy)phenyl pyridine carboxylate ligands show wider mesophase ranges and more varied phase behavior than the imines 63. A rule of thumb proposed for *these* complexes was that the smaller the volume of the counterion, the broader the mesophase range and the lower the melting point; however, these guidelines need to be modified for the stilbazole complexes.



63: X = BF_4, CF_3SO_3; n = 1–10, 12, 14, 16



64: X = BF_4, CF_3SO_3, NO_3, PF_6; n = 2, 4, 6, 10, 14

The silver(I) thiolates $Ag(SC_nH_{2n+1})$, 65, n = 4, 6, 8, 10, 12, 16, and 18,[93] show lamellar phases, cubic phases, and micellar phases (Figure 19). With increasing chain length, the lamellar and cubic phase ranges decrease and the micellar phase becomes predominant. X-ray diffraction has shown that the micellar phase for n = 18 possesses a columnar hexagonal ordering, arising from the rearrangement of the solid-state (layer) to cyclic $(AgSR)_8$ structures. It is proposed that a μ^3- to

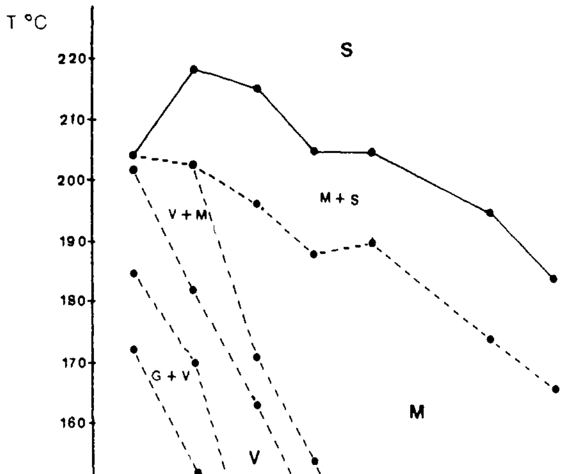


Figure 19. Transition tempertaures of the silver thiolate $AgSC_nH_{2n+1}$ complexes 65 and a function of the chain length n [C, crystal; G, lamellar (S_A); V, cubic; M, micellar; S, amorphous]. (Reprinted from ref 93. Copyright 1990 American Chemical Society.)

μ^2-SR bond rearrangement occurs on transition from the cubic to the micellar phase.

$$Ag—S—C_nH_{2n+1}$$

65: $n = 4, 6, 8, 10, 12, 16, 18$

C. Gold

The yellow-orange gold(III) (alkyloxy)dithiobenzoates **66** (Ar = $C_nH_{2n+1}OC_6H_4$) were prepared by the following reaction sequence:

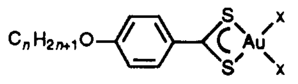
$$AuCl(tht) + NaS_2CAr \rightarrow Au_2(S_2CAr)_2$$

$$Au_2(S_2CAr)_2 + X_2 \rightarrow 2AuX_2(S_2Ar)$$

66 (X = Br, Cl)

$$AuX_2(S_2CAr) + MeMgI \rightarrow Au(Me)_2(S_2CAr)$$

The complexes **66** (n = 8, 10, X = Cl, Br) showed S_A phases at around 150 °C, while **66** (n = 10, X = Me) showed the same phase already at 60 °C; all the complexes decomposed on reaching the clearing points, 40–50 °C higher, except for the dimethyl complex which decomposed at 130 °C.[15a,24]

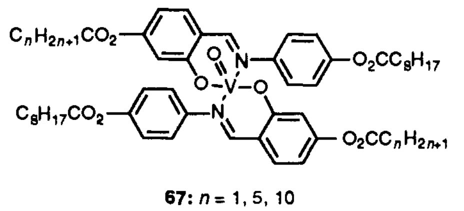


66

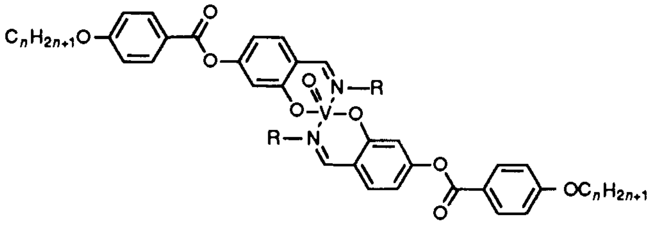
IV. Other Metals

A. Vanadium

All the presently known vanadium metallomesogens contain the vanadyl (V=O) group and hence are paramagnetic with V(IV) (d^1). The first complexes, **67**, made by Galyametdinov et al.,[94] showed S_C phases and were of particular interest since they had low viscosity in the mesophase and thus could be oriented easily by a magnetic field. Studies on the related complexes **68** (n = 10), by Serrano et al.,[95] noted that the transition temperatures for R = alkyl are considerably lower than for the Cu and Pd analogs. X-ray studies carried out in a magnetic field[14] have shown that the vanadyl complexes have a positive magnetic susceptibility and that the molecules interdigitate in the phase. ESR studies of **68** (n = 10, R = C_5H_{11}) have been carried out[96] and it was found that the N-alkyl complexes aligned with the magnetic field and that the alignment persisted into the solid state. By contrast, complex **68** (n = 10, R = $C_6H_4OC_5H_{11}$) also aligned with the field in the nematic phase, but lost its orientation at lower temperatures. It was suggested that stronger intermolecular interactions here tended to reduce the ability of the molecules to align with the external field.



67: n = 1, 5, 10



68: R = C_5H_{11}, $C_{10}H_{21}$, C_6H_4OMe, n = 10
R = C_3H_7, n = 5–12, 14, 16, 18

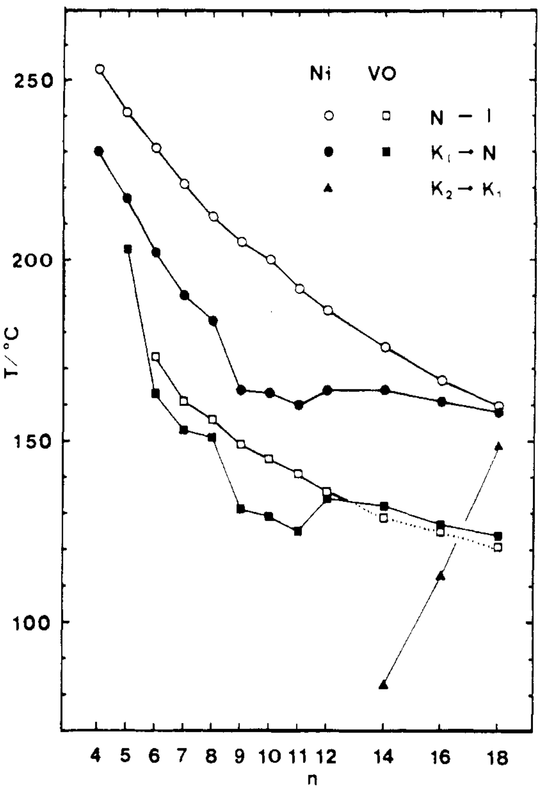


Figure 20. Phase diagram showing the transition temperatures for the (salicylaldminato)nickel and oxovanadium complexes **4** and **68**, with change in chain length, n. (Reprinted from ref 11. Copyright 1991 American Chemical Society.)

Hoshino et al.[11] have synthesized the similar nematogenic compounds **68** (R = C_3H_7), varying the length of the end chain, n, while keeping the lateral n-propyl-N chain constant. They found that the vanadyl complexes had lower transition temperatures and shorter nematic ranges than the corresponding Ni complexes (Figure 20). The vanadyl center in the system is square pyramidal, this increases intermolecular separation and consequently the T_{NI} for this series is lower than for the square planar Cu and Ni systems. However, it was suggested that the axial interactions (V–O···V–O) become dominant in the solid state, and so melting points are not much lower than for the Cu series. The copper materials, in turn, have lower transition temperatures than their nickel analogs and this again is thought to be related to the fact that they are more susceptible to tetrahedral distortion, thus disturbing the planarity of the system. An analysis of the ESR spectra of the vanadyl complex, dissolved in its Ni(II) nematic host congener, indicated the central core to be highly oriented.[14]

An imaginative recent paper from the laboratory of Swager[97] has used the observation (see ref 1), that many

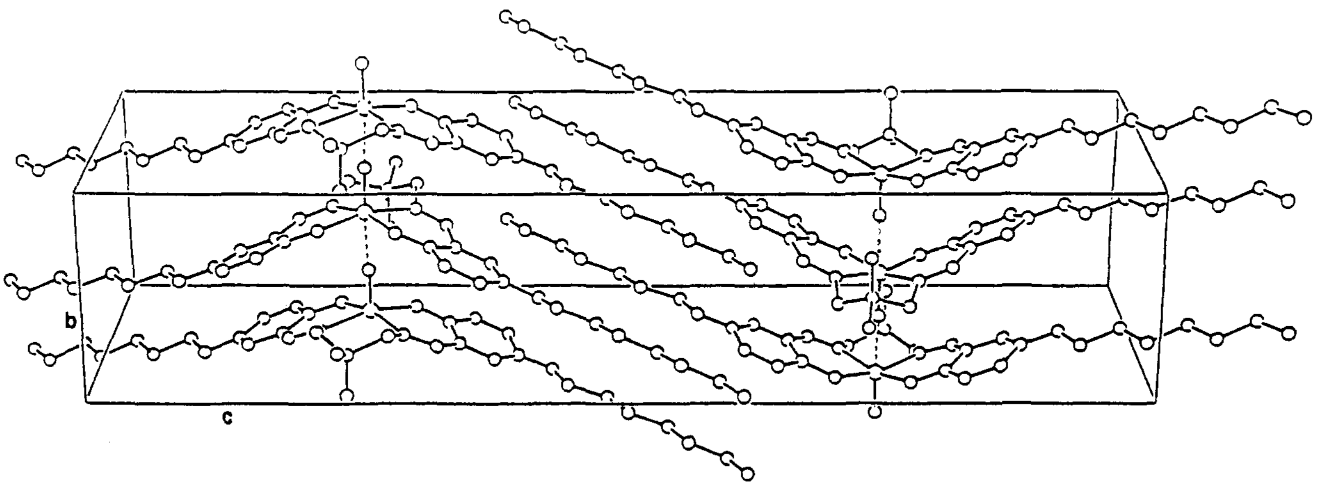
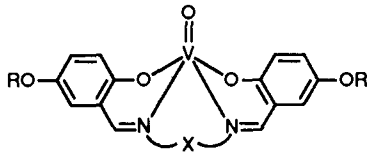


Figure 21. An ORTEP drawing of the unit cell of 7(Me$_2$salpn)VO viewed approximately down the *a* axis, showing the V=O···V=O interactions. (Reprinted from ref 97. Copyright 1992 American Chemical Society.)

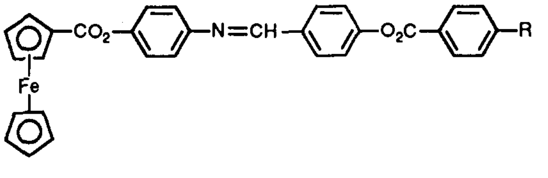
metallomesogens appear to associate in the mesophase via intermolecular dative bonds, to demonstrate chain structures in some vanadyl Schiff base complexes. Thus the *n*-(salen)VO complexes **69a** (X = CH_2CH_2; R = C_nH_{2n+1}, *n* = 4–12) form smectic phases and the IR spectra, ν(VO), indicate that the molecules are monomeric. By contrast, the *n*-(salpn)VO complexes **69b** are not liquid crystalline and the IR spectra indicate that they associate via V=O···V=O··· links into chains. The *n*-(Me$_2$salpn)VO (**69c**, X = $CH_2CMe_2CH_2$; R = C_nH_{2n+1}, *n* = 5–14) show very interesting intermediate properties. They possess chain structures in the crystalline solid, confirmed by an X-ray determination, which demonstrates that the molecules pack in a highly interdigitated layered structure (Figure 21). DSC and optical microscopy studies indicate that the complexes (R = C_nH_{2n+1}, *n* = 6–8, 10, 12, 14) show smectic phases, which the IR spectra identify to still contain V=O··· V=O··· chain structures. However, the IR data are consistent with a disassembling of the chains once the isotropic phase has been reached (>171 °C).[97]



69a: X = CH_2CH_2
b: X = $CH_2CH_2CH_2$
c: X = $CH_2CMe_2CH_2$

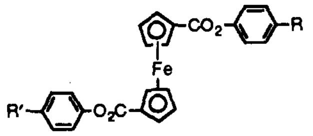
B. Iron

Although the smectogenic ferrocenyl Schiff bases **70** were the first well-characterized organotransition metallomesogens,[6] there have been surprisingly few reports on further iron compounds until a short time ago.[98]

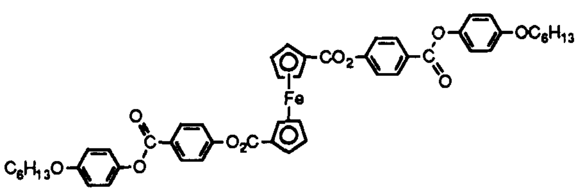


70: R = C_nH_{2n+1}, *n* = 5, 6, 8
R = OC_nH_{2n+1}, *n* = 8,10

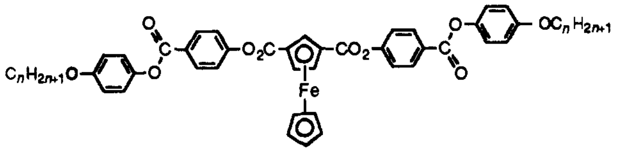
A recent publication has reported mesophases for compounds **71a** and **71b**,[99a] derived from ferrocene-1,1′-dicarboxylic acid, but only a 1:4 mixture of the two shows true liquid crystal behavior, with a nematic phase seen between 110 and 170 °C. The ferrocene **72a**, also derived from ferrocene-1,1′-dicarboxylic acid, exhibited no liquid crystalline properties on heating, while that with 4-(decyloxy)-4′-cyanobiphenyl esters, Fe{$C_5H_4CO_2(CH_2)_{10}OC_6H_4C_6H_4CN$}$_2$, showed complex melting behavior and evidence for a short-range smectic phase.[99b] By contrast, those derived from the ferrocene-1,3-dicarboxylic acid, **72b–e**, showed high-temperature nematic phases[100] with reasonable ranges (34–64 °C, Table VI).



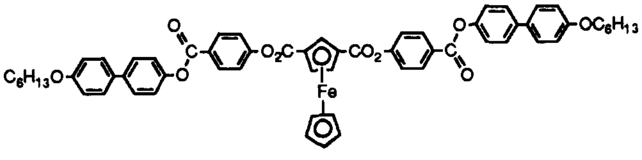
71a: R = R′ = $OC_{10}H_{25}$
b: R = $OC_{10}H_{25}$, R′ = OH



72a



72b: *n* = 6, 7, 8



72c

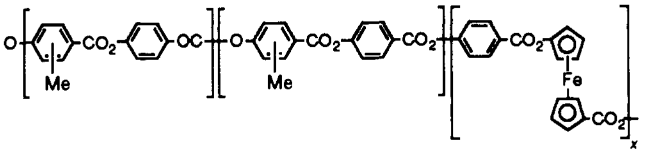
A nematogenic ferrocene polymer **73** has also been reported.[101] Comparison with the polymer without the ferrocene unit, showed that the ferrocene was actually

Table VI. Mesogenic Ferrocenes (72)[100]

complex	phase transition	T, °C
72a	K-I	172
	(I-N)	(153)[a]
72b	K-N	184
	N-I	248
72c	K-N	183
	N-I	217
72d	K-N	172
	N-I	206
72e	K-N	204
	N-I	235

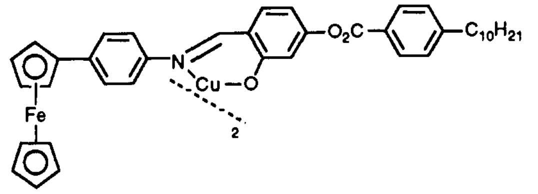
[a] Monotropic transition.

inducing mesomorphism into the nonmesomorphic polymer system.



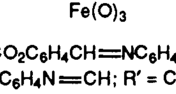
73

Another interesting ferrocene compound is the mixed metal ferrocene/copper salicylaldimine complex **74** reported by Galyametdinov et al.[102] This is the first example of a heteronuclear liquid crystalline metal complex.



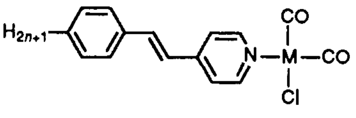
74

Ziminski and Malthête[103] have reported two series of butadiene iron tricarbonyl complexes **75a** and **75b**. Those with R = methyl and R′ a phenyl ester, on the butadiene, **75a**, showed nematic phases, while those with R = an imino function and R′ a phenyl ester, **75b**, showed S_A as well as nematic phases, and at very significantly lower temperatures. The enantiomers could act as dopants inducing ferroelectricity when dissolved in a nonchiral S_A or S_C phase.

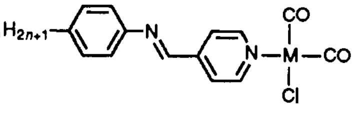


75a: R = Me; R′ = $CO_2C_6H_4CH{=}NC_6H_4C_8H_{17}$
b: R = $C_nH_{2n+1}OC_6H_4N{=}CH$; R′ = $C_nH_{2n+1}OC_6H_4O_2C$

C. Rhodium and Iridium



76: M = Rh, Ir; $n = 5-12$



77: M = Rh, Ir; $n = 5-12$

The unsymmetrical mesomorphic complexes **76** and **77** have been made by the groups in Sheffield and Zaragoza; much of their chemistry has already been reviewed.[1] The stilbazole complexes, $M(CO)_2Cl(n\text{-}OST)$ (**76**, M = Rh or Ir), had fairly low transition temperatures. The rhodium complexes melted into nematic phases at temperatures ranging from 110 to 123 °C for $n = 5-8$, and into an S_A phase for $n \geq 7$, at around 85 °C; the clearing into the isotropic was accompanied by substantial decomposition.[104] Bruce et al. found that the iridium analogs behaved very similarly, but were thermally more robust. In the solid state the iridium complexes were a deep burgundy color, which changed to a bright yellow on melting into the mesophase. This is probably due to a stacking in the solid (via Ir···Ir interactions) which breaks down in the mesophase. By contrast, the rhodium complexes were bright yellow and showed no color changes. The iridium (alkyloxy)stilbazole complexes show mean polarizabilities α, about twice those for the free ligand (ca. $(60 \pm 6) \times 10^{40}$ against ca. $(35 \pm 4) \times 10^{40}\ J^{-1}\ C^2\ m^2$), indicating that the metal causes a very large increase in polarizability.[105] There is a similarly large increase in the polarizability anisotropy. The birefringence Δn of the *n*-octyloxy complex was 0.18.[23] It was found that the introduction of a fluorine at either the 3- or the 2-position of the stilbazole ligand destabilized the phases and no mesophase behavior was seen for the substituted materials.

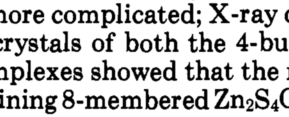
Serrano and his collaborators have used the related (phenylimino)pyridine (*n*-OIP) to form closely analogous mesomorphic complexes, $M(CO)_2Cl(n\text{-}OIP)$ (**77**, M = Rh or Ir), which showed nematic and S_A phases.[106]

D. Zinc, Cadmium, and Mercury

1. Zinc Complexes

The zinc bis[4-(alkyloxy)dithiobenzoates] [$\{Zn(S_2CC_6H_4OC_nH_{2n+1})_2\}_m$] were obtained as red crystals which showed a nematic phase for $n = 4-7$, and in addition, a S_C phase for $n \geq 8$ (monotropic for $n = 8$).[15a] The material obtained from the synthesis, prior to recrystallization, was an orange powder, also mesomorphic but showing two immiscible phases, one nematic and the other a S_C phase.

A single-crystal X-ray structure determination of the *un*substituted zinc dithiobenzoate itself shows it to be monomeric (**78**) with the two pairs of sulfurs approximately tetrahedral about the metal.[107] However, the mesomorphic zinc bis[4-(alkyloxy)dithiobenzoates] proved to be more complicated; X-ray determinations of single red crystals of both the 4-butyloxy and the 4-octyloxy complexes showed that the molecules were dimeric, containing 8-membered $Zn_2S_4C_2$ rings, formed by the fusion of two ZnS_2C rings, and in which the geometry about zinc approximated to trigonal bipyramidal (**79** and Figure 22).[15a] Furthermore, EXAFS data for the octyloxy complex clearly indicate that the



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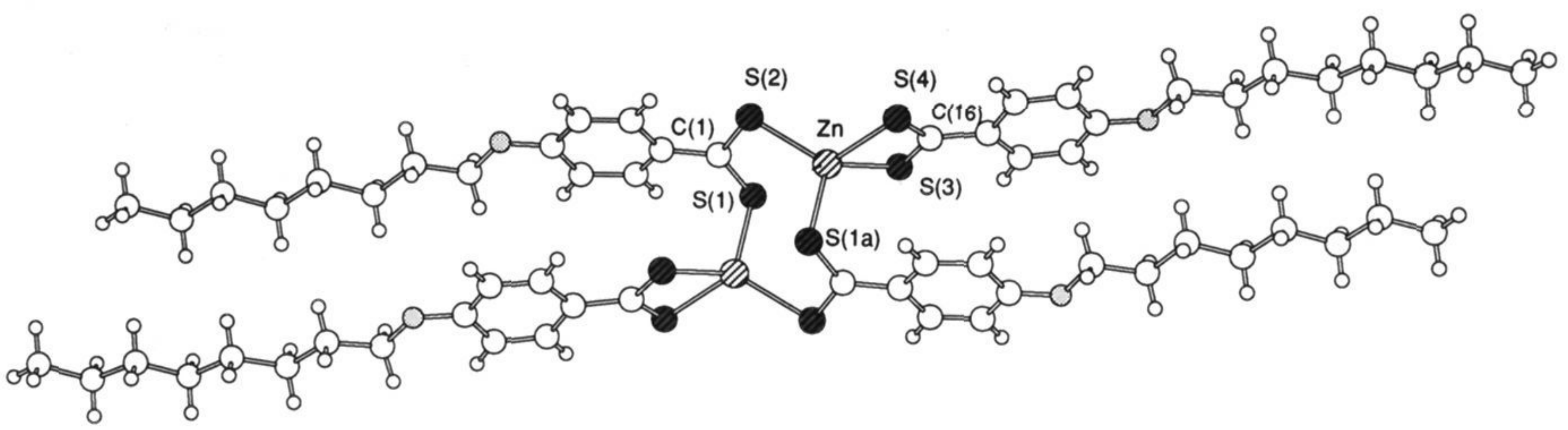


Figure 22. X-ray structure of the dimeric zinc bis[4-(octyloxy)dithiobenzoate] complex **79**.

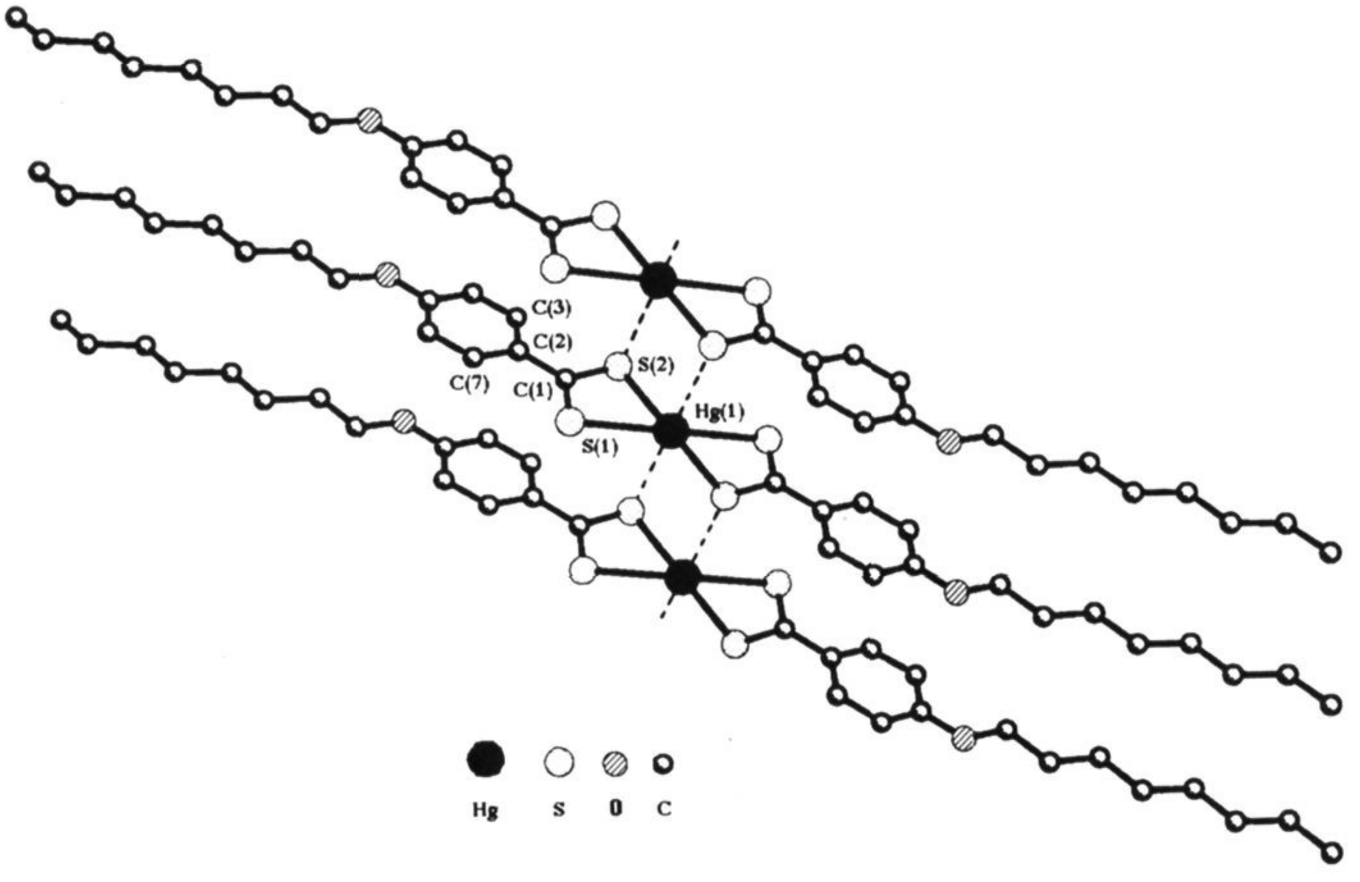
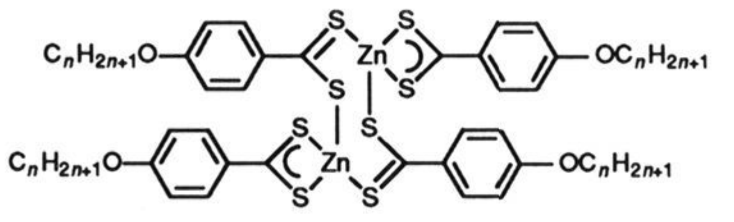


Figure 23. X-ray structure of the mercury bis[4-(octyloxy)dithiobenzoate] complex showing the distorted octahedral coordination about the metal with the long axial interactions.

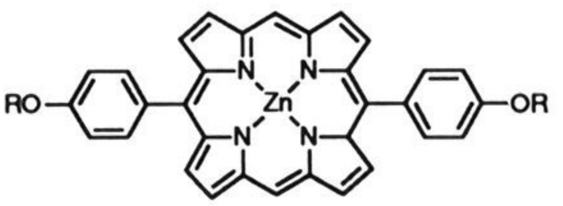
same structures are in the nematic mesophase as in the red crystals and the orange powder; thus the three near-neighbor Zn–S distances are 2.35, 2.50, and 2.85 Å, both at ambient and at 160 °C.[108] Thus the molecules are not tetrahedral about the metal, and the dimeric structure persists into the mesophase.



79

It has already been noted that mesomorphism in metallomesogens seems to be incompatible with a tetrahedral geometry about the central metal.[1] Another example of this was reported by Hoshino et al.[69] who found that the zinc analogs of the mesomorphic copper salicylaldimines **47** were not liquid crystalline; zinc salicyladimines are tetrahedral.

Bruce et al. have recently shown that the 5,15-bis(alkyloxyphenyl)porphinatozinc complexes **80** (n = 8, 10, 12, 14, 16), showed crystal smectic B phases, by optical microscopy.[109] Since porphyrins, having flat, disklike geometries, normally show discotic phases,[1] this shows that phase types, even of complex molecules, can be changed by relatively small molecular alterations.



80

2. Cadmium and Mercury Complexes

Mesomorphic cadmium and mercury bis-alkoxydithiobenzoates, analogous to the zinc complexes, have also been made. The structures of the cadmium *complexes are not known and the mesomorphism has* been only partly defined, as it is composed of coexistent immiscible red (nematic) and yellow (S_C) phases for n = 4–10.[110] Red crystals of the mercury complexes could be obtained and single-crystal X-ray determinations of both $Hg(S_2CC_6H_4OC_4H_9)_2$ and $Hg(S_2CC_6H_4OC_8H_{17})_2$ were carried out. These showed (Figure 23) the mercury atoms to have a basically planar coordination, with one sulfur of each chelate much closer (2.432, 2.412 Å) than the other trans pair (2.913, 2.96 Å), and with long, axial coordination to two further sulfurs of two adjacent molecules (at 3.209, 3.362 Å). This gave an overall strongly distorted octahedral geometry to each mercury.[110] The mercury complexes were again mesomorphic and showed textures apparently due to the presence of immiscible nematic and S_C phases.

E. Lead

The lead carboxylates $Pb(C_nH_{2n+1}COO)_2$ (n = 5, 7, 9, 11, 13, 15, and 17 and n = 10)[111] were reported to show S_C phases and S_A phases for $n > 5$ as well as a more ordered smectic phase at lower temperatures.[112] More recently, lead(II) alkadiynoates (**81**) have been synthesized,[113] which showed smectic phases over wide temperature ranges and glassy mesophases at lower temperatures.

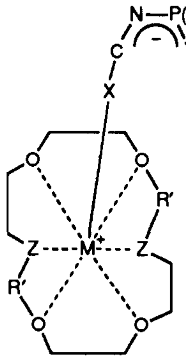
$$(CH_3—(CH_2)_m—C\equiv C—C\equiv C—(CH_2)_n—COO^-)_2Pb^{2+}$$

81: m = 5, 7, 9; n = 2
m = 5, 7; n = 8
m = 9; n = 9

F. Alkali and Alkaline Earth Metals

It is well known that alkali and alkaline earth carboxylates can form thermotropic as well as lyotropic phases on heating in the anhydrous state.[114] These materials usually show lamellar phases with the alkyl chains becoming more and more disordered as the temperature is raised. The polar heads then lose order and may aggregate to form lamellar or ribbon- or disklike phases. Recent work on calcium tetradecanoate[115] has also reported the occurrence of cylinders in the melt, above 180 °C.

Salts of the alkali metals, sodium and potassium, with N-phosphorylated amides and thioamides complexed to the crown ethers 15-crown-5, 18-crown-6, dibenzo-18-crown-6, and diaza-18-crown-6 (**82**) have been synthesized. They show smectic phases with a fan-shaped texture by microscopy.[116] These phases have been found to be electrically conducting, which, together with the low transition temperatures (Table VII), gives great potential for applications.



82: R = C_3H_7, CH_3; R′ = CH_2CH_2
R = C_3H_7; R′ = o-C_6H_4;
X and Y = S, O
M = K, Na
Z = O, NH

G. Rare Earths

Although discotic lutecium phthalocyanine complexes are well known and have been discussed,[1] only in 1991 did Galyametdinov et al.,[117] report calamitic salicylaldimine complexes of europium, gadolinium, dysprosium, and praseodymium of formula MX_2L_3 (L = $C_7H_{15}OC_6H_4COOC_6H_3(OH)CHNC_{12}H_{25}$; X = Cl or NO_3). These compounds show an unidentified smectic phase.

Table VII. Phase Behavior of Some Complexes of Crown Ether *N*-Phosphorylated Amides and Thioamides 82

M	X	Y	Z	transition temperatures, °C
			R = C_3H_7, R′ = CH_2CH_2	
K	S	S	NH	K 128 S 140 I
K	O	O	NH	K 105 S 130 I
K	S	O	NH	K 100 S 125 I
Na	O	O	O	K 35 S 80 I
Na	O	O	NH	K 80 S 99 I
Na	O	S	O	K 100 S 124 I
Na	O	S	NH	K 80 S 105 I
			R = CH_3, R′ = CH_2CH_2	
Na	O	O	O	K 25 S 80 I

V. Conclusion

The range of the metallomesogens is expanding rapidly,[118] as was foreshadowed in ref 1. Relationships between the molecular structures and the physical properties continue to clarify but fuller understanding still awaits the investigation of a greater number of species. However it is already clear that the phase behavior of metallomesogens is often dominated by the ligands. In discotics the metal is frequently so hidden in the molecule that it appears to have little influence on the mesomorphism. Although this effect is less pronounced for the calamitic mesomorphs, even there large ligands can cause the formation of metallomesogen phase types very similar to those seen for the ligands themselves.

A number of different geometries about the metal center are compatible with calamitic mesomorphism, including linear, square planar, and 5-coordinate. However, there are so far no clearly defined examples of tetrahedral or octahedral calamitic metal centers.

A major consequence of incorporating a metal is to increase the transition temperatures over those for the free ligands. This can have undesirable consequences for potential applications, and thus significant effort has been expended to develop methods for reducing them. Several approaches have been successful. (1) Melting points (but not the clearing temperatures) are reduced on mixing two related complexes, thus increasing the mesophase range. For many applications the use of mixtures poses no problems. (2) The replacement of hard anions or anionic ligands (e.g. chloride) by softer ones (long chain carboxylates or long chain sulfates) markedly decreases the phase transition temperatures. Metallomesogens incorporating amphiphiles thus have great potential. (3) Since, in general, molecules pack less easily when they are less symmetrical, this makes crystallization more difficult, and hence can reduce the melting temperature. Thus an unsymmetrical complex, with two or more different ligands, will often have a significantly lower melting temperature than a symmetrical one.

In addition to such approaches, it is also possible to decrease the melting points by appropriate lateral substitution of the ligand; however, the effect is very dependent on the nature and the position of the substituent.

Metallomesogens have contributed to a modification of liquid crystal thinking, since they provide evidence for the formation of thermotropic mesophases by ionic salts. The work reviewed here includes many new examples, and shows how widespread this phenomenon is; thus we must conclude that Coulombic ionic attractions do not cancel out the generally much weaker, dipole–dipole and van der Waals, forces normally responsible for mesophase behavior. Indeed, in the metallomesogens that have been studied they may actually enhance mesomorphism.

A parallel indication is that the X-ray structures of single crystals show that a substantial number of mesomorphic compounds actually exhibit axial intermolecular ligand-metal dative interactions. This phenomenon has already been used to advantage, for example, in the new liquid crystalline polymeric vanadyl–Schiff base complexes (section IV.A), where the stacking is carried by $V{=}O \cdots V{=}O$ interactions which do not interfere with the mesomorphism.

Such intermolecular dative interactions are harder to incorporate in the structures of tetrahedral complexes and there is increasing evidence that tetrahedral geometries about the metal centers repress mesomorph formation. The same may be expected to apply to octahedral geometries, but there has been little opportunity to test the suggestion as very few potentially calamitic complexes incorporating octahedral metal centers have yet been made. When mesomorph formation is "forced" on a molecule, distortions can occur; thus when the normally tetrahedral zinc bis-dithiobenzoates are made mesomorphic by the addition of *p,p'*-alkyloxy chains, they dimerize in the solid to give structures with 5-coordinate zincs in eight-membered $\overline{\text{Zn–S–C–S–Zn–S–C–S}}$ structures (section IV.D). It might be supposed that these dimeric structures would split in the mesophase, especially since they do so in solution in organic solvents. However, the EXAFS evidence is against that and indicates that the eight-membered ring dimers persist in the mesophase. Other evidence too, indicates that many intermolecular contacts present in the crystals are retained in the mesophases.[1]

It is plausible that the absence of such interactions for tetrahedral metal centers, which cannot accept an intermolecular donor without distortion from the tetrahedral geometry, may be the limiting factor there.

It is clear that, provided certain precautions are followed, many metals of the periodic table can be incorporated into mesogenic complexes. For success it is necessary to ensure that (a) transition temperatures are not excessive and (b) the reactivity normally associated with the metal center in a complex, is also repressed, perhaps by selective shielding. By this means, it should be possible to include the full range of optical, electronic, magnetic, and geometric characteristics of the metal.

Many different ligand types are available for the construction of metallomesogens. They include monodentate (such as the pyridines) and bidentate (such as salicylaldimines, dithiobenzoates, and the cyclometalates). Obviously many more will be brought into use. The chief requirements are that the ligands bind well to the metals and that they contain several (at least two) para-substituted aromatic groups, as well as one long (generally $>C_{10}$) alkyl or alkyloxy chain. This gives the overall rodlike shape to the ligand.

The actual phases obtained in calamitic metallomesogens tend, on the whole, to follow the trends already found for organics. Thus the shapes characteristic for S_C phases are also seen in the metallomesogens. It is frequently found that the lower members of a homologous series will show nematic, while the higher ones will show smectic behavior.

One very interesting recent development is the realization that thermotropic mesomorphic compounds are not limited to just rod- or disklike shapes. This also applies to metallomesogens, where there is considerable evidence that many molecular shapes can be mesomorphic, for instance book and P shapes. There is also strong evidence in favor of the existence of a continuum of phase types between the rod- and disklike shapes, as for example, in the elliptical bis biphenyl copper β-diketonates **43**. Although they have the molecular shapes of disklike molecules, they show calamitic phase types. A further example is a recently reported bis-phthalocyanine bearing 12 (2-ethylhexyl)oxy side chains and containing two coppers, which forms mesophases, probably of nematic type.[119] In this region of structural ambiguity one would expect to find molecules that give rise to biaxial mesophases and which could lead to very fast switching effects. One such system has already been claimed,[47] and clearly there is considerable scope for further imaginative synthetic chemistry.

Notes Added in Proof

(i) A copper complex which shows a chiral smectic C mesophase and ferroelectric properties has been made. It is based on structure **55** with $n = 10$ and $R = n\text{-}C_4H_9O_2CC^*HMeO_2CCH{=}CHC_6H_4\text{–}$, the chiral substituent being derived from (–)-butyl L-lactate. This complex shows switching times in the millisecond range (similar to that of the ligand alone); this is an improvement on earlier ferroelectric metallomesogens,[33] but longer than many conventional organic ferroelectrics, which switch in the microsecond range. The vanadyl analog shows similar properties. (Marcos, M.; Serrano, J. L.; Sierra, T.; Gimenez, M. J. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1471.

(ii) The use of metallomesogens in directed stereoselective catalysis is an intriguing possibility. The application of bulk mesomorphic materials for this purpose is complicated by their anisotropic optical properties (which make optical measurements difficult), their cost, and their poor solubility properties. Thus an indirect approach has been developed in which slim, rodlike ligands are used to guide reactions. This has been applied to the rhodium-catalyzed hydroformylation of 1-hexene. The rodlike phosphite ligands, $RC(CH_2O)_3P$ (especially for $R = CH_2O_2CC_6H_{13}$), showed high regioselectivity toward the formation of $n\text{-}C_6H_{13}CHO$, by comparison with both normal and bulky phosphine- or phosphite-based ligands. (Poelsma, S. N.; Maitlis, P. M. *J. Organomet. Chem.* **1993**, in press.)

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