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Liquid crystal properties of metal–salicylaldimine complexes. Chemical modifications towards lower symmetry[1]

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Contents

Abstract

A body of work involving liquid crystalline phases in the family of transition metal complexes of salicylaldimines has been reviewed. An account is given as to how the mesophases can be derived from archetypical coordination compounds in the liquid state by an approach of lowering symmetry. Attention is confined to reported examples of well-established metal–salicylaldimine mesogens. Firstly, it is shown that the nematic behavior can be related to the molecular shape anisotropy as a primary factor, which works advantageously to generate the orientational order. A group of bis[4-(4-alkoxy)benzoyloxy-*N*-alkylsalicylaldiminato]metal

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complexes represents the nematics. Smectic fluctuations in, and eventual ordering of, the nematic phases are treated together, and several other effects conducive to this tailoring of phase property are pointed out. Pure smectic phases are found in bis[4-alkoxy-*N*-arylsalicylaldiminato]metal complexes. The change in the rigid core shape and the packing considerations for the terminal alkyl chain substituents are discussed in relation to the positional ordering. The literature is cited to shed light on the increased biaxial character of the molecular structure possibly leading to unusual local ordering. Finally, columnar phases in complexes of [M(salen)] type with heavily incorporated long alkyl chains are introduced and contrasted to simpler dialkylated derivatives which are smectogenic.

Keywords: Metallomesogen; Liquid crystal; Metal complex; Salicylaldimine

1. Introduction

A research field involving metallomesogens [1,2] has evolved explosively since the mid-1980s. The preceding decade saw a steady increase in interest towards liquid crystals incorporating transition metal elements, and the recognition of great potential as advanced molecular materials with this new class of liquid crystals [2] attracted more researchers into the field. As a result, whereas early syntheses of these contemporary metallomesogens [3,4] relied on relatively simple ligands including cyanobiphenyls, which are representative of conventional liquid crystals, some 30 different types of ligand, most of the d-block elements, and even some lanthanide elements have now been incorporated in reported mesogenic complexes. The structural diversity covering coordination numbers from 2 to 8 is tremendous, and some of them are beyond what is achievable with pure organics. Quite a few reviews and accounts have registered this evolution process as well as more on the history [1,2,5–10].

Thus, metallomesogens are no longer exotic modifications of liquid crystalline compounds, but a distinctive class of transition metal complexes with which we are able to pursue novel physical properties in the anisotropic fluid environment. It is important to develop suitable new applications, and such studies have also been set out. Meanwhile, it is desirable to extract general principles that underlie the vast variety in the examples, as potential new workers should not be restricted by the empiricism. This article attempts to devise some logical terms for doing so. The literature citation is limited, therefore, to those (not all) involving low molecular weight metal–salicylaldimine complexes, the liquid crystal phases in which have been well established. Some results obtained and recently refined in our laboratory are also reported.

2. Mesomorphism

A brief description of the liquid crystalline state is given first for the sake of reference in this article. The reader will find more details in specialized review texts for the fundamentals [11], chemical aspects [12,13], and the background physics [14,15].

Liquid crystals are states of matter intermediate between the solid and the liquid.

Fig. 1 provides snapshot images of nematic (N), smectic A (SmA), and smectic C (SmC) liquid crystals. Constituent objects (complex molecules for our purpose) are drawn here as featureless rods, indicating that *we assume* that they rotate freely about their long axes. These systems comprising rod-like building blocks are called calamitic. These states emerge either by cooling from the isotropic (ordinary) liquid or by heating from the crystalline state, and thus are called thermotropic liquid crystals. Polymorphs occur in the sequence shown along the temperature parameter.

From a physicist's view, liquid crystals are systems in which "a liquid-like order exists at least in one direction of space and in which some degree of anisotropy is present" [14]. We can imagine, starting with a familiar crystal, that a liquid crystal is formed by imposing positional order in, rather than three dimensions (3D), two dimensions (2D) or one dimension (1D) or no order at all (0D). The nematic and smectic phases have 0D and 1D positional orders, respectively. Fig. 1 includes a schematic of a discotic hexagonal disordered (D_{hd}) phase as an example of columnar phases with 2D positional order, together with a discotic nematic (N_D) phase which also comprises disc-like entities.

Orientational freezing is another way of yielding anisotropy. Thus, starting with an isotropic liquid state, a nematic phase is obtained by aligning rod-like molecules with their long axes (and disc-like molecules with their short axes) parallel to each other. The time and ensemble average of the directions of orientation is denoted by

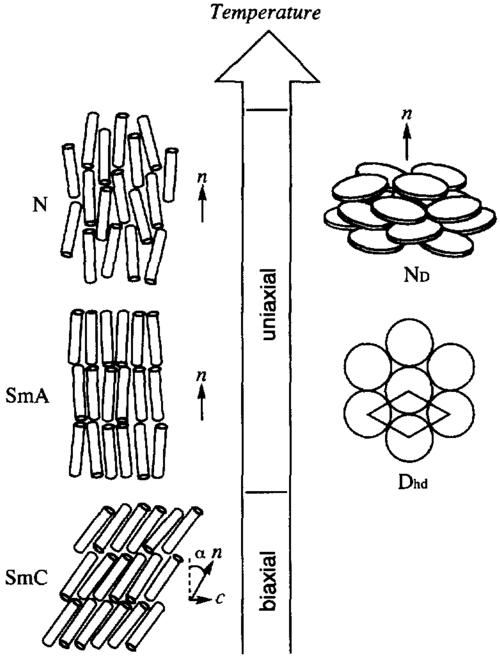


Fig. 1. Schematic representations of N, SmA, SmC, N_D, and D_{hd} liquid crystals. Note that a top view of six liquid-like columns is given for the last phase.

the vector ***n*** (called *director*) in Fig. 1. The orientational order can be described by the parameter

$$S=\langle P_2(\cos\theta)\rangle=\tfrac{1}{2}\langle 3\cos^2\theta-1\rangle$$

in which θ is the angle between the director and a specified principal axis of an individual molecule and the angle brackets indicate the averaging.

Both of the liquid crystal and plastic crystal phases are classified as mesophases. Constituents are orientationally disordered while maintaining the three-dimensional crystal lattice in the latter. Ambiguous phases exist where molecular fragments, such as flexible alkyl tails, are conformationally disordered but the metal complex moieties are still positionally ordered in all three dimensions. These partially disordered crystal phases should be identified on the basis of crystallography before compounds exhibiting them are called mesomorphic. Only those highly disordered liquid crystal phases shown in Fig. 1 will be considered below, even though the term mesophase is used for its simplicity. The mesogenic molecules are normally far from spherical and often produce multiple solid polymorphs. Their coexistence in a given sample need not be a concern and should rather be carefully characterized, if one wishes to relate it to the mesomorphic properties. A reference to the thermodynamic considerations [16] may be useful when complicated phase behaviors involving metastable phases are encountered.

Crystal structures are thus governed by a number of interactions, among which the short-range steric interactions can be decisive [17]. Although the molecular interactions necessary to form mesophases may be manifested in the crystalline state, an inverse approach (from the liquid state down) is deliberately chosen in this article in order to keep in mind that the molecules are in highly excited motional states in the liquid crystals. We will occasionally digress to examine the crystallographic information for certain structural aspects.

3. Principles in designing mesomorphic complexes

It would be convenient to pick an example of a liquid coordination compound and to demonstrate the design pathway to mesomorphic derivatives. Metal chelates of Schiff base ligands [18, 19] are widely known and would serve as a most illustrative example. In fact salicylaldimines have been favorably employed in the synthesis of metallomesogens [1], and the efforts can now be rationalized as follows. We are not concerned at this moment with what has actually guided the reported work, which will be reviewed later.

A liquid state archetypical complex is shown in Fig. 2; in an old report it is found that the copper(II) and nickel(II) complexes of *N*-(*n*-alkyl)salicylaldimines can be modified to melt at temperatures as low as 57 °C and 87 °C, respectively, by extending the linear alkyl group up to the *n*-tetradecyl group [20]. With this clue in hand, our strategy is to extend the rigid fragment just enough to induce the orientational order. Chemical modifications actually applied are typified by the introduction of a 4-substituted benzoyloxy group in the 4-position of the salicylidene moiety, which

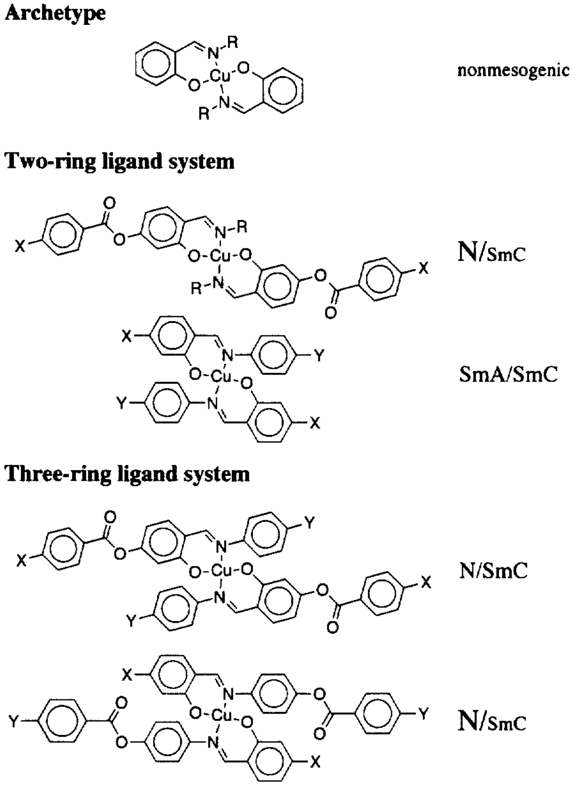


Fig. 2. Chemical modifications of the liquid-state archetypical complex to mesomorphic derivatives for metal–salicylaldimine systems.

results in elongated complexes (exemplified by copper(II) complexes in Fig. 2) of a two-ring ligand system. Associated phase symbols N/SmC in Fig. 2 indicate that these mesophase types have been revealed. Insertion of a *p*-phenylene group in the *N*-*n*-alkyl moiety is another readily performed modification which would generate a still elongated, but rather wide and flat, core structure. Actual examples have emerged showing smectic phases with the aid of terminal substitution by alkoxy (X) chains. If these two modifications are combined into the three-ring ligand systems, elongated and enlarged complexes result. Studies have shown that the mesophase pattern with this group of compounds returns to the mixed N/SmC type, reflecting the primary importance of the shape factor.

The scheme in Fig. 2 sums up the basic trend in the calamitic mesomorphism of metal–salicylaldimine complexes. Chemical manipulations for liquid crystals must be performed so as to enhance anisotropy in the intermolecular forces, while adjusting their strength to suppress the three-dimensional crystal ordering. The shape elongation was merely a most obvious approach in the above example. Situations may occur where appropriate archetypical species cannot be found or where the desired shape cannot be achieved owing to chemical feasibility reasons, or because various functional groups have to be incorporated for certain material properties, and so on. Therefore, more general guidelines would be useful when one has to start from scratch. A list of interactions to be considered for thermotropic metallomesogens is now given.

3.1. The anisotropy in the molecular shape

This is the primary factor of concern with liquid crystals and provides a most convenient strategy for either elongating or flattening the molecule. Since it has been shown theoretically that the repulsive steric interaction alone drives such molecules into orientationally ordered arrangements based on the excluded volume effect [14,15], we might as well take advantage of it. Not only the packing entropy is maximized in this way, but also even isotropic attractive interactions can stabilize the anisotropic liquid due to the anisotropic nature of the pair distribution function [11]. The "shape" implies the overall molecular shape effective in the liquid crystal phase; an intuitive view of a metallomesogenic molecule as consisting of a metal core which tends to order and the flexible alkyl grouping which brings in disorder would be only partially valid.

3.2. Intermolecular attractive interactions

The system is held together by van der Waals interactions, although they are sometimes treated implicitly. Dispersion force has been identified as having the greatest significance in explaining the anisotropic attractive interactions necessary to form the nematic liquid crystal [11]. Thus, enhancing the anisotropy in the molecular polarizability would be an effective approach. The dipole/induced-dipole interaction contributes to the formation of the tilted SmC phase [21]. The dipole/dipole interaction is often neglected, particularly for the nematic state. Coordinate bonds are more or less polarized and metallomesogens will contain many other polarized bonds, such as carbonyloxy and azomethine groups. The effects of polarization may be significant if these bonds are arranged in a non-centrosymmetric manner and the molecules do not rotate as freely as in the models. However, it is difficult at present to identify manifestations of the dipole/dipole interaction and they may be discussed only in relative terms with appropriate non-polar reference systems.

3.3. The axial coordinative interaction

Interactions such as metal–metal or metal–ligand bonding are directional and often anisotropic. The unsaturation in 4-coordinate square-planar complexes, for instance, can be utilized to promote the molecules to interact along the axial direction. Even when the molecule has less anisotropic shape, this additional interaction would favor the formation of a one-dimensional array of the molecules. Examples of lantern-shaped metal–alkanoate dimers which in fact form columnar liquid crystals represent such cases [22]. This is a stronger interaction over a relatively short range and must be tamed so that the system does not solidify as a coordination polymer. Note that the interactions in the alkanoate systems are dynamic; it has been shown by a ^{13}C NMR investigation on dirhodium tetranonanoate that in its columnar mesophase a metal center hops around over four oxygen sites in the neighboring dimer [22]. It is difficult to factor out the influence of bonding interactions in the cases of calamitic metallomesogens, the physical model for which assumes a free molecular rotation about an axis perpendicular to the interacting direction.

3.4. Peripheral designs

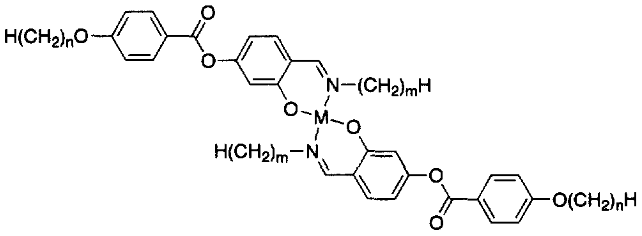
This is meant to refer to the peripheral shaping of molecules with otherwise highly symmetrical coordination spheres. For example, the immediate cubic symmetry in the octahedral coordination geometry does not appear to fit easily to anisotropic arrangements by the use of the aforementioned interactions. Reports do exist, however, on columnar liquid crystals of metal(III) tris-chelates of β-diketonate ligands [23,24]. They are attached with heavily alkyl-substituted phenyl groups and the columnar association of these molecules may occur along their C_3 axes. Apart from these unusual phases, no low molecular weight mesomorphic (neither calamitic nor columnar) complexes of cubic coordination spheres are known to date. We have recently attempted to synthesize disc-like species of a cubane-like Cu_4O_4 core using dimeric copper(II) complexes of 2-(*N*-salicylideneamino)ethanol derivatives, but the materials obtained turned only to disordered crystals prior to thermal decomposition [25].

4. Liquid crystal behavior of metal–salicylaldimine complexes

4.1. Nematics

As mentioned in Section 3, induction of the orientational and/or positional order in the liquid of bis[*N*-(*n*-alkyl)salicylaldiminato]copper(II) has been achieved in several ways. The first type of elongated complex is designated below by **M1**-*n.m*. A particular homologue will be specified, when necessary, by the metal atom (or a central metal group) **M**, and the number of carbon atoms *n* and *m* in the alkoxy and alkylimino groups, respectively; a homologous series will be referred to by its span, though not always fully covered.

The nematogenic character of a wide series of copper(II) complexes, **Cu1**-1.*m* ($m=4$–18), **Cu1**-6.*m* ($m=3$–13), and **Cu1**-*n*.3 ($n=4$–18) was revealed in our work [26,27]. Fig. 3 presents a "phase pattern diagram" for the first series **Cu1**-1.*m*, in which the phase transition temperatures have been plotted against *m* (labels K and I denote crystalline and isotropic liquid phases, respectively). Comparison of such phase patterns over series of compounds, rather than of phase transitions in a homologue of arbitrary choice, would provide a better view of the ordering and



M1-*n.m*

stability characteristics of individual structural types, since the core–core interactions are delineated by a gradual change in the number of methylene units serving as a weak perturbation. Furthermore, misinterpretation of the results owing to an accidental anomaly in certain alkyl homologues (either legitimate or spurious) may be avoided in this way. The incorporation of 4-methoxybenzoyloxy groups to the archetypical species is sufficient to stabilize the N phases relative to the K phases throughout the region $4 \leqslant m \leqslant 18$, while melting temperatures have also been raised inevitably by the substitution. The diagram also shows that the extension of "lateral" chains brings down the N–I phase transition temperature T_{NI} gradually and the N phase area is bounded by a falling curve on the top. Similar behavior has been found for the effect of "terminal" chains in the series **Cu1**-*n*.3 [27], a *T*–*n* phase pattern diagram for which is given in Fig. 4.

Other homologous series of **Cu1**-*n.m* were studied by Sirigu and coworkers [28–30] and by Marcos and coworkers [31–33]. Available data for T_{NI} have been compiled in Figs. 5 and 6. We now leave the K phases aside, since they do not necessarily represent common polymorphs. Unfortunately, the experimental data

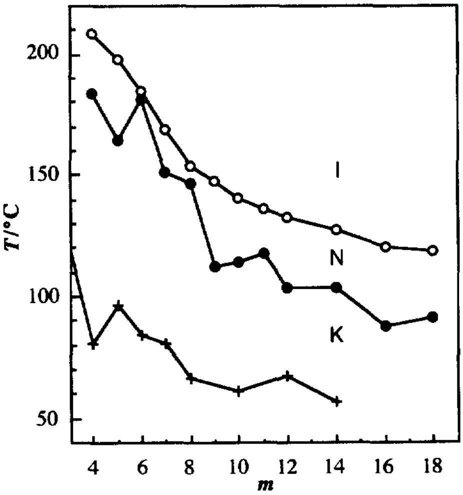


Fig. 3. Phase pattern diagram for series **Cu1**-1.*m*. Melting points (+) of bis[*N*-(*n*-alkyl)salicylaldiminato]copper(II) complexes [20] are also plotted for comparison.

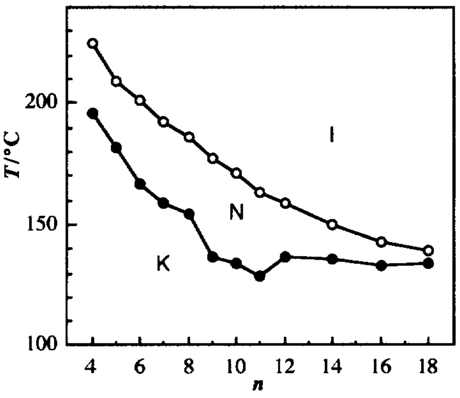


Fig. 4. Phase pattern diagram for series **Cul-*n*.3** (adapted from Ref. [27]).

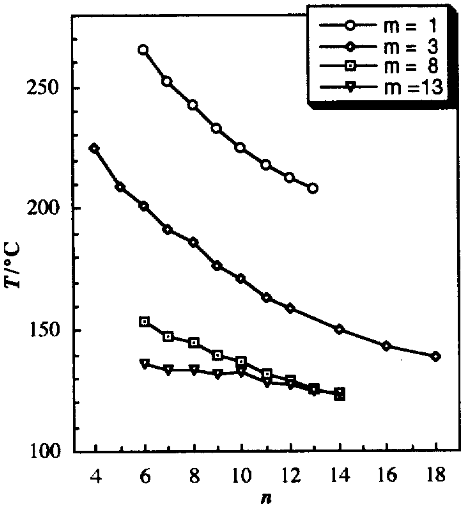


Fig. 5. Comparison of T_{NI} curves for series **Cul-*n*.1**, **Cul-*n*.3**, **Cul-*n*.8**, and **Cul-*n*.13** (adapted from Refs. [27,28,30]).

are not sufficient to define fully the surface of the N phase domain in three-dimensional *T–n–m* space, but we may still analyze the effect of the length of either terminal (*n*) or lateral (*m*) alkyl chains on the thermal stability of the N phases using these plots. There appears to be a sharp drop in T_{NI} as we begin to increase m ($m = 1 \rightarrow 3$) regardless of *n*, and the plot of T_{NI} *vs* *n* at $m = 3$ defines a smooth falling curve similar to the one at $m = 1$, but in a temperature range lowered by about 60 °C (Fig. 5). In Fig. 6 one can see that the differential $(\partial T_{NI}/\partial m)_n$ soon levels, and more quickly so with larger *n*. On the other hand, the differential $(\partial T_{NI}/\partial n)_m$ is also negative and apparently always so for $m \leq 7$; but, on increasing *m* further, a positive slope starts to appear somewhere in the region $1 < n < 6$. Thus, the two kinds of

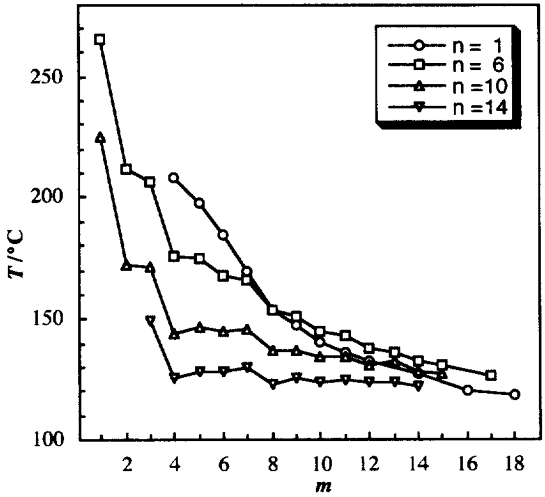


Fig. 6. Comparison of T_{NI} curves for series **Cul-1.*m***, **Cul-6.*m***, **Cul-10.*m***, and **Cul-14.*m*** (adapted from Refs. [26,29,30]).

chain seem to work differently when they begin to extend. Their effects on the values of T_{NI} are, however, not too different from each other once they grow intermediate in size, and the values tend to converge at very large *n* and *m* around 120–130 °C.

The effect of the alkyl tail length on the T_{NI} curve relations has been discussed for organic nematogens [12]; the gradual falling trends in high T_{NI} values can be explained basically by the interplay between the dispersion force and the packing entropy under the influence of chain flexing. Odd–even alternation of the T_{NI} curve is often observed among organic mesogens. A basic trend in the present observations (except for the lack of the odd–even effect in *n*) may be explained in the same way. The complex **Cul-*n.m*** can thus be regarded as two nematogenic molecules with their rigid cores joined near end-to-end (most of the ligands possess N phases by themselves).

Then the *N*-alkyl groups are laid more or less along the rigid core part and sterically shielded, and more of the attractive part of their interactions will contribute to the nematic stability. A statement by Sirigu and coworkers that "the alkanamino terminals appear to be somewhat efficient stabilizers of the mesophase than the alkoxy ones" [30] is in accord with this situation. Their comparison was made between sets of data, and for ones with higher *m* underlying SmC phases were detected. This is illustrated in Fig. 7, which shows schematic contours of T_{CN}/T_{NI} (T_{CN} is SmC–N transition temperature) projected onto the *nm* plane. The effect is not diagonally (*n vs m*) symmetric judged from the data collected to date, and hence the N phases in their comparison may well reflect different influences of the smectic fluctuations. At any rate, the T_{NI} values of **Cul-n_1.m_1** and **Cul-m_1.n_1** differ by only several degrees, and the asymmetry seems to be weaker than in SmC–N (or I) transition temperatures from intermediate *n* and *m* onwards.

Imbalance in the tail length alerts us to steric considerations. Polishchuk and

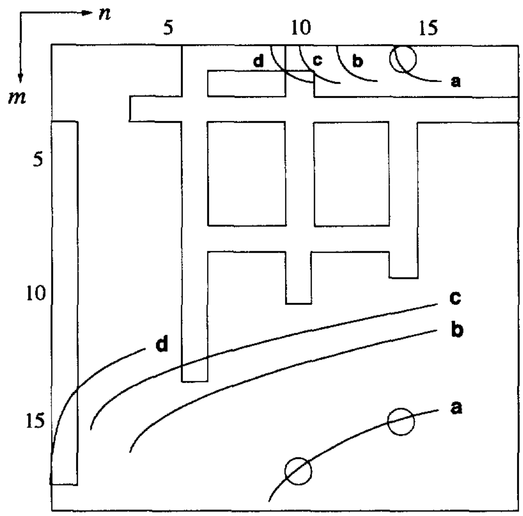
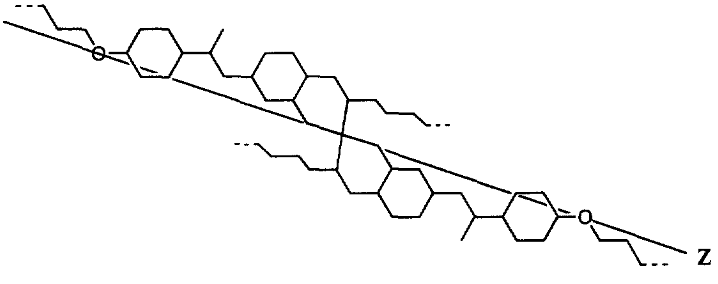


Fig. 7. A schematic projection onto the nm plane of the SmC phase domain (below N) for complexes **Cu1**-$n.m$. Contours of (a) $T_{CN}/T_{NI} = 1.00$, (b) 0.97, (c) 0.94, and (d) 0.91, estimated from the data reported to date, are given. Purely nematogenic homologues (as reported) are indicated by squaring their sites, and three circled homologues on curve (a) are pure smectogens.

Timofeeva [8] have pointed out that the strong projection-hollow type of packing allows various intermolecular contacts, whereby the crystal phase "jumps over" smectic mesophases and is interfaced directly to the nematic phase. The fact that the complexes **Cu1**-$n.m$ ($m = 3$–9, and possibly $m = 2$ as well) are pure nematogens regardless of n may also be related to steric irregularity in the rigid core group.

It is surely a crude approximation that the complex **M1**-$n.m$ behaves as a uniaxially cylindrical object, however they rotate, but it is indeed a difficult problem how to find or realistically define the principal axes of inertia for modeling the rotational state. In our determination of the orientational order parameter S in the N phases of **Ni1**-11.3 [34], the molecular long axis z was assumed to run through the terminal oxo groups in an open configuration, as shown below.



Two sets of the results, one obtained from the ^{1}H NMR experiment with a neat sample of **Ni1**-11.3 and the other from the EPR spin probe experiment using its

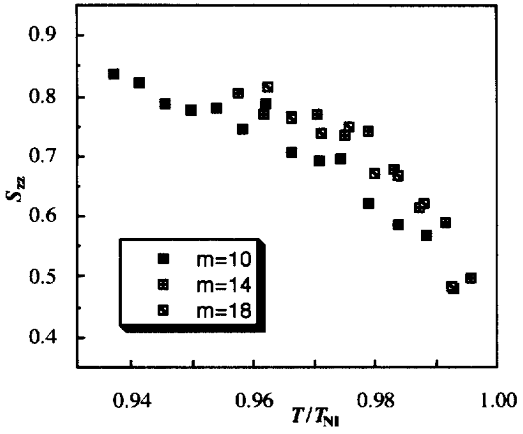


Fig. 8. Nematic orientational order parameter S_{zz} for selected homologues of **Ni1**-1.*m* determined by the ^1H NMR experiments. The molecular long axis (*z*) is defined as shown in the text.

congener **VO1**-11.3, showed a discrepancy which is traceable to the assumptions made to simplify the analysis. The study was later extended to the methoxy derivatives **Ni1**-1.*m* ($m = 10$, 14, 18), for which the above assumption should be valid [35]. Consistency in the results improved considerably. In fact, the three homologues yielded similar values for the order parameter (Fig. 8), and corresponding spin probes **VO1**-1.*m* ($m = 10$, 14, and 18) showed nearly invariant ordering features. Thus, these lateral long alkyl chains seem to be rather disordered in the N phases, whereas the terminal alkyl groups contribute more to the nematic order.

Lateral steric intrusion in the molecular structure is expectedly detrimental to the nematic stability. Marcos and coworkers reported a study on complexes **Cu1**′-10.*m*; these are isomeric to **Cu1**-10.*m* with the benzoyloxy moiety moved from the 4- to the 5-position of the salicylidene group [36]. The effect of the *N*-*n*-alkyl chains as unshielded, truly lateral groups is well illustrated here; the N phase area for the 5-isomers reduces by some 70 °C compared with the 4-isomers over a region $3 \leqslant m \leqslant 9$.

Apical steric intrusion and tetrahedral distortion are also somewhat harmful. The phase pattern diagrams for series **M1**-*n*.3 (**M** = Ni, Cu, VO; $n = 6$–18) can be inspected to check this; the N phases shift down upon switching the metal atom from Ni to Cu, and then to VO [34]. The decrement in T_{NI} is nearly independent of *n* and $\Delta T_{NI}(\text{Ni–Cu}) = 27$ °C and $\Delta T_{NI}(\text{Cu–VO}) = 25$ °C, respectively, on the average over $6 \leqslant n \leqslant 18$. These results are interpreted in terms of the difference in planarity of the chelate core structure. Note that the comparison is being made in a region on the *nm* plane where the mesophase is purely nematic (for copper(II) complexes at least) and the T_{NI} curve has a common functional shape with *n* among the three series.

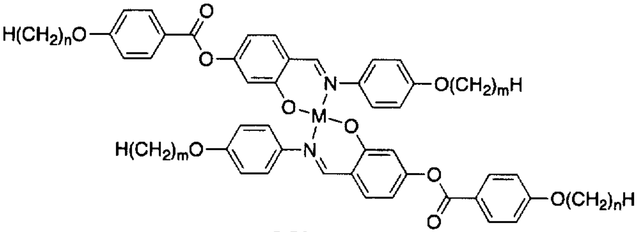
A square-planar structure is normally assumed for nickel(II)–salicylaldimine chelates, but cases with static deformation towards tetrahedral varieties have been well documented [19]. Griesar *et al.* reported on the paramagnetism of chiral nematic

(N*) phases of **Ni1**-7.5* and **Ni1**-12.5*, which are analogous to **Ni1**-7.4 and **Ni1**-12.4 with a chiral methyl branch introduced in the β-position of the *N*-*n*-butyl group [37]. The authors interpreted the results as being due to the tetrahedral species. Whereas the diamagnetic (square planar) fraction in the green solid of **Ni1**-7.5* was estimated to be 0.78, the population of the proposed tetrahedral species in the N* phase was not determined because of the inseparable effect of alignment in the magnetic field. At any rate, the fact is that the nematic order surely survives. The stability of a firmly square-planar geometry has been related favorably to the high thermal stability of the N phases of some homologues of **Pd1**-*n.m* [30].

We now proceed to examine the effect of the axial interactions. *N*-Methyl and ethyl homologues **Cu1**-*n.m* ($m=1$, 2) have been left out of the above discussion on the effect of alkyl chain length on T_{NI}. The Italian group found only an SmC phase for **Cu1**-14.1 and no mesophase for **Cu1**-14.2 [28,30]. It is likely that the latter was due to the metastability of any mesophase relative to its K phase and, as is shown in Fig. 7, the apparent irregularity is due to the isolated occurrence of an SmC phase domain in the upper right edge of the diagram. The SmC phases of **Cu1**-14.1 and **Cu1**-14.15 have different structural features [30]; this has been demonstrated also for the smectic C fluctuations in the N phases of **Cu1**-10.1 and **Cu1**-10.10 [33], suggesting that the interactions leading to the formation of two SmC phase domains in Fig. 7 are different in nature. The aforementioned report on the 5-isomers **Cu1′**-10.*m* [36] also illustrates how quickly the SmC phase (below N) in the *N*-methyl complex **Cu1′**-10.1 is eliminated by extending the lateral group. Molecular packing considerations were presented by the authors [1,33]. The axial interaction of the type Cu–O···Cu–O··· could also be considered as a driving force to positional ordering, since these *N*-methyl complexes have a rather exposed chelate core. It is curious why the smectic phases (or fluctuations) of **M1**-*n.m* generally involve the molecular tilt, and the axial interaction seems to be a contributing factor.

A rather exceptional case in this light is a rare chloroiron(III) complex **FeCl1**-7.12 reported to exhibit an SmA phase [38] over a temperature range where its congener **Cu1**-7.12 would show its N phase. The SmA phase behavior was also described for **FeCl1**-10′.12, an analogue of **FeCl1**-10.12 with 4-decyl instead of 4-decyloxy termini [39]. The driving force for the orthogonal smectic ordering is not clear, but the report also tells that μ-oxo dimerization of **FeCl1**-10′.12 partly restores the nematic behavior [39].

Complexes of a three-ring ligand system, denoted as **M2**-*n.m* below, can be regarded as stronger mesogens joined at more nearly a side-by-side position. The basic mesomorphic features in **M1**-*n.m* having a high length/breadth ratio are inherited and thus the major phase types are N/SmC (at least among **Cu2**-*n.m*). Not as many homologous series as for the type **M1**-*n.m* have been studied, but the N phases have been found over generally higher temperature ranges in accord with the increased size in the molecular rigid core. Smectic C behavior is clearly enhanced; the phase pattern diagram shown in Fig. 9 for series **Cu2**-*n*.2 ($n=6$–18) [40], in which a higher (larger *n*) part of the mesophase area is occupied by the SmC area, is illustrative when compared with one for the series **Cu1**-*n*.3 in Fig. 4. Since corresponding ligands in this case are still purely nematogenic (except for the highest homologue of $n=18$), it is necessary to consider new factors for the complexes.



M2-*n.m*

The SmC-promoting effect of the inserted *p*-phenyleneoxy groups would be more evident on *T–m* plots. The lateral alkyl series **M2-10.*m*** ($m=1$–14) were investigated by Marcos *et al.* [41]. A phase pattern diagram for **Cu2-10.*m*** with an available data set shows the dominance of the SmC area. The purely nematic range is limited now to only two cases of $m=1$ and 2. A stable SmC phase starts to appear even with propoxy lateral groups, whereas it takes the *N*-undecyl chains ($m=11$) in the four-ring complex **Cu1-10.*m*** (Fig. 7); the effect of a *p*-phenyleneoxy group is worth eight methylene units in this regard. Differences due to the kind of metal center were also described by the Spanish group. One can check with their data that the delimiting curve for the N phase area for series **VO2-10.*m*** [42] lies nearly parallel to that for series **Cu2-10.*m***. In contrast, a depression of some 40 °C can be seen for series **FeCl2-10.*m*** [43]. A further depression by about 20 °C is notable for complexes **Ni2-10.*m***, and only the lowest four homologues ($m=1$–4) barely show the upper edge of their N phase area [41]. As far as the SmC phases are concerned, those in **VO2-10.*m***

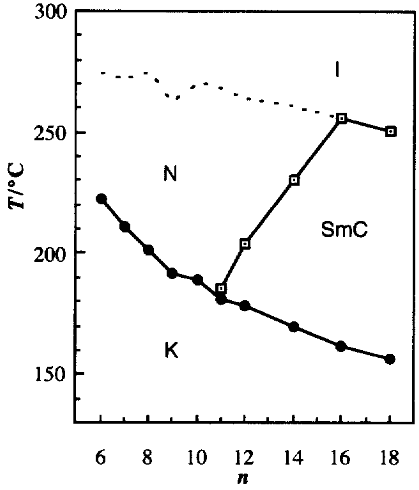


Fig. 9. Phase pattern diagram for series **Cu2-*n*.2**. Dashed line indicates isotropization temperatures with extensive decomposition (adapted from Ref. [40]).

seem to be masked by a so-called crystal smectic phase area and those in **FeCl2**-10.*m* appear to be located in much lowered temperature ranges. Copper(II) complexes **Cu2**-10.*m* have the lowest melting temperatures insensitive to *m*, thus displaying the largest area of stable mesophases N/SmC among the complexes studied.

These features could be interpreted to reflect various modulations in the intermolecular interactions as follows.

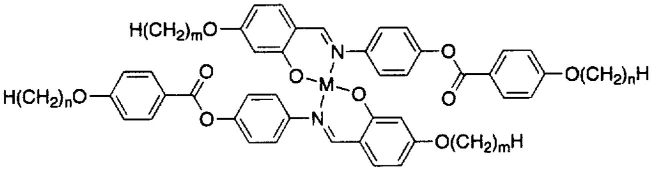
(1) The static tetrahedral distortion typical of bis[*N*-arylsalicylaldiminato]-nickel(II) derivatives seems to be a serious steric disadvantage for their N phases. Partial positional ordering at lower temperatures is also difficult and the molecules quickly order into three-dimensional crystals, which are in fact more stable than those of copper(II) congeners. The distortion seems to be dynamic in nature in the case of copper(II) complexes. We have demonstrated for **Cu2**-4.6′, an analogue of **Cu2**-4.6 with hexyl instead of hexyloxy lateral chains, that the chelate planes form a dihedral angle of 22° in its crystal, but the overall lath-like shape is well maintained [40]. It can be easily imagined that the excluded volume effect would not be affected too much by the square-planar↔tetrahedral conversion over small amplitudes.

(2) A square-pyramidal coordination geometry ought to be unfavorable for both N and SmC phases. The case of chloroiron(III) species is an illustrative example, but the effect seems to be fully compensated in the oxovanadium(IV) complexes. The counteracting positive effect is likely to be the axial coordinative interactions enhanced for these *N*-aryl derivatives and the complexes must be in a cooperative motional state in order for this effect to be operative in the N phases. The emergence of more-ordered smectic phases in place of the SmC phases of copper(II) congeners may be an associated feature.

(3) The extruding oxo group may be somewhat shielded sterically by the *N*-phenylene grouping, but this should be the case for the apical chloro ligand as well. The lowered thermal stability of the N phases in chloroiron(III) complexes has been alternatively explained by the authors invoking trigonal-bipyramidal distortion in the metal coordination geometry [1].

In reference to the effect of polarized bonds in the molecule, the literature data are not systematic enough to allow for a reasonable analysis. With regard to those in remote positions, series of complexes **Cu2′**-10.*m* ($m = 1–10$) and **VO2′**-10.*m* ($m = 1–10$) have been studied [44]; these are analogous to **Cu2**-10.*m* and **VO2**-10.*m* but containing methyleneoxy (instead of carbonyloxy) linkers in the ligand. It can be seen by comparing their phase pattern diagrams that upon such replacement the mesophase area shifts down by 40–70 °C (more at smaller *m*) and with the SmC area being pushed to the right ($m \geqslant 5$ or 6) a new SmA area occupies the nearly left half of the mesophase area. Thus the nematic behavior has been completely lost. The whole behavior is apparently dominated by a drastic change in the flexing characteristics of the linker. It is desirable to test with non-polar *and* rigid linking groups (such as ethylene, if feasible). The effect of polar groups has also been studied with another mobile ring, and derivatives with the *N*-phenyl ring substituted by F, CF_3, and CN groups have been reported [45]. Use of such a strongly polar group as CN in place of the methoxy terminal group in **Cu2**-10.1 again leads to a nearly complete masking of the N phase by an SmA phase [45,46].

Little attention has been paid to the other type of three-ring ligand modification giving rise to complexes **M3**-*n.m* shown below. Early reports on **Cu3**-7.12 [47] and on an analogous complex [1,48] tell us that they display N phases. We investigated related complexes **Cu3**-*n*.x ($n = 6$–18; x indicates that the salicylidene moiety is unsubstituted) over a terminal alkyl series and confirmed the nematogenic property [49]. In only one homologue, **Cu3**-12.12, carrying four long chains have we so far observed an SmC phase. It appeared that a potential SmC phase area existed behind a wide K area on the phase pattern diagram for the series **Cu3**-*n*.x. Melting temperatures were lowered in this case by replacing the central metal atom by the oxovanadium(IV) group, but no smectic phases were revealed in the resulting series **VO3**-*n*.x. These compounds are more representative of end-to-end fused twins of three-ring mesogens, and the nematic behavior is more or less guaranteed. However, the unsubstituted compounds in particular seem to be more susceptible to chemical degradation due to a weakened in-plane ligand field, which would make it worse by raising the melting points via promoted axial interactions in conjunction with the projection-hollow packing. Therefore, the chemical adjustment of the mesomorphic phase behavior of these complexes and the interpretation of its consequences would be more laborious than for other systems.



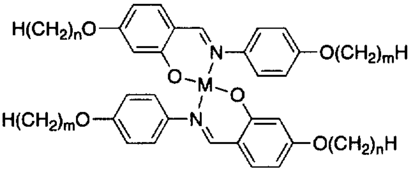
M3-*n.m*

In summing up this subsection, the advantage of molecular shape anisotropy in the metallonematic property has been highlighted; a rigid core is of primary importance for the nematic ordering, lateral chains for the thermal stability and smectic C fluctuations, and terminal chains for both. The interactions involved do not differ too much from organics, qualitatively speaking, and the explanations based on the repulsive steric and the attractive van der Waals forces may be applied. However, the steric factors are far more complicated than in conventional nematogens. "Elongated" is an ambiguous expression and the problem of shape irregularity needs to be borne in mind. Signs of the axial interactions possibly effective in certain nematic phases have been pointed out. It must be clear by now that we are in need of more information on the actual rotational dynamics.

4.2. Smectics

Complexes of *N*-salicylideneanilines can be derivatized simply by attaching 4,4′-dialkoxy substituents to the two-ring ligand to produce metallosmectogens **M4**-*n.m*. Whereas previous work has been repeatedly reviewed, it is acknowledged again that, in retrospect, the reports by Ovchinnikov and coworkers on this group of complexes served as an initiator for the whole line of research activities with metal–salicylaldimine mesogens [6].

The complexes **M4**-*n.m*, in which two mesogenic ligands are now joined side-by-side, have an overall "brick-like" molecular shape. The crystallographic information on the previous six-ring complex **Cu2**-4.6′ provides a measure of the decrease in molecular length; longitudinal spans over the terminal (alkoxy) oxygen atoms and over (benzoyloxy) oxygen atoms are 25.1 Å and 13.0 Å, respectively (benzoyl rings form dihedral angles of 68° and 83° to respective salicylidene rings, i.e. not in the open conformation) [40]. While the difference will be compensated by attached alkyl tails, short homologues of the present four-ring complexes are still close to the limit of the Onsager model (repulsive force alone) assuming a breadth of about 9 Å. In the event, the orientational freezing always accompanies positional ordering, and the mesophases observed so far are invariably smectics. One might expect from the molecular shape with increased biaxiality that unusual biaxial phases might be formed. "Elongated" homologues ($n > m$) exhibit only SmA phases, which have so far been regarded as uniaxial, whereas an SmC polymorph is often observed with complexes carrying long alkyl chains. The phase type characteristic of this group is thus SmA/SmC. This smectic C ordering differs from that treated in Section 4.1. When we enter into an SmC phase through an SmA phase, the transition is usually of second order, whereas either SmC–N or SmC–I transitions involve a latent heat.



M4-*n.m*

A phase pattern diagram for series **Cu4**-*n*.2 ($n = 3$–18) [50] is given in Fig. 10 as an example. Comparison with one of the series **Cu1**-*n*.3 ($n = 4$–18) of similar chemical

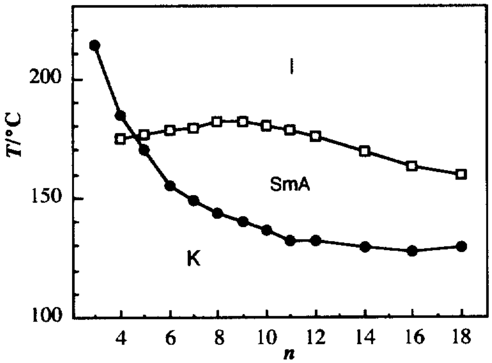
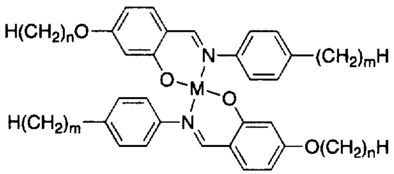


Fig. 10. Phase pattern diagram for series **Cu4**-*n*.2 (adapted from Ref. [50]).

composition illustrates how the N phase area in the latter is replaced by the SmA area in the former. The SmA–I transition temperature T_{AI} curve shows upward convection with a maximum of about 180 °C for an intermediate length of the terminal alkyl tails ($n = 8$–10). Still the SmA phase boundary is rather flat on the top, whereas the K phase limit rises sharply as the series descends. This hampers detection of possible SmA phases in **Cu4**-*n*.2 ($n < 4$).

Literature data concerning these types of complex **Cu4**-*n.m* [51–54] are not fine enough to map the surface of the SmA phase domain in the *T*–*n*–*m* space. It is conceivable, however, that the position of its maximum projected on the *nm* plane shifts towards smaller *n* as we ascend along *m*, with its value changing little, and the diagonal asymmetry is recognized again in the region of smaller *n* and *m*. The fact that the range of *n* with positive differential $(\partial T_{AI}/\partial m)_n$ is wider than the range of *m* with positive $(\partial T_{AI}/\partial n)_m$ is indicative of a somewhat disturbing effect on the SmA phase of long lateral chains attached to the more mobile fraction of the molecule. Apart from this subtle difference, the thermal stability of the SmA phases in complexes **Cu4**-*n.m* seems to be not too sensitive to the length of either chain and the values of T_{AI} appear to converge around 130 °C along the diagonal. The underlying SmC domain cannot be defined clearly at this moment.

A number of modifications of **M4**-*n.m* are found in the literature which provide insights into the modulations in the intermolecular interactions necessary to form the SmA and SmC phases. First of all, a contribution of the outboard dipole moment associated with the ether linkage is highlighted by comparing with a short series of complexes **M5**-12.*m* ($m = 1$–8) synthesized by Ghedini and coworkers using 4-alkylanilines [55–57]. Whereas the SmA phase area appears to shift down by only about 10 °C, judging from the difference between the T_{AI} values for **Cu4**-12.6 and **Cu5**-12.6, the SmC phases are definitely destabilized to the extent of becoming undetectable (except with $n = m = 14$) by the elimination of the oxo groups.



M5-*n.m*

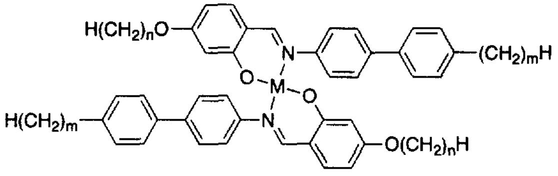
Incorporation of other metal centers has been tested from early times [58]. The oxovanadium(IV) center works positively with these two-ring *N*-aryl ligands, and a short series **VO5**-12.*m* ($m = 4$–8) [59] displayed its SmA phase area with its delimiting line lifted by 15–25 °C relative to **Cu5**-12.*m*. The comparison also holds true between the alkoxy versions **VO4**-12.6 and **Cu4**-12.6. Recalling the trend in T_{NI} with six-ring complexes **M2**-*n.m* showing similarity between M = VO and Cu, it can be deduced that the apical oxo group must be well shielded again here and, furthermore, a positive effect of the axial interaction induces enhanced stability in the SmA phases in **VO4**-*n.m* and **VO5**-*n.m*. This in turn suggests that the molecules packed now in layers must execute more cooperative rotations. Melting temperatures are, in general, also raised.

Among other metals, palladium atoms seem to raise T_{AI} by 40–45 °C, deduced from a comparison between **Cu4**-7.*m* and **Pd4**-7.*m* ($m=6$, 10) [60], and this has been explained by the geometrical rigidity of palladium chelate. However, part of this increment should come simply by virtue of the palladium atom being a heavier metal; SmC and K phases are also stabilized by 20 °C and 40–45 °C, respectively. Crystal structures of **Cu4**-7.6 [61] and **Pd4**-7.6 [62] have been solved. The palladium(II) complex adopts a centrosymmetric square-planar coordination geometry and this leads in fact to a tighter packing into a crystal of space group $P2_1/a$ ($Z=2$), whereas a crystal of the copper(II) complex contains the same form together with molecules of overall C_2 symmetry ($P\bar{1}$, $Z=3$). However, even the former palladium(II) complex deforms in the crystal in such a way as to make "a dihedral angle of 27° between the least-square plane of salicylideneaminato moiety and the coordination plane" [62]. Therefore, one should not overestimate the effect of a rigid coordination sphere alone.

The tetrahedral distortion in copper(II) complexes must again be of dynamic nature, and they also seem to fit fairly well to the smectic phases, as long as the planar state is populated sufficiently to maintain the anisotropic environment. Moreover, a little instability to such distortion could be an advantage, and relatively low melting temperatures of smectogenic copper(II) complexes may be appreciated in this light. On the other hand, the lack of stable mesophases in **M4**-7.8 (**M**=Zn, Co, Ni) [58] and **Co4**-7.1 and **Ni4**-7.1 [8] has been ascribed to their firm tetrahedral geometry. Coexistence of square-planar and tetrahedral species was demonstrated by the EPR spectra of both a single crystal of **Cu4**-7.1 [63] and an SmA liquid crystal of **Cu4**-7.8 [58] by Russian groups. Microscopic segregation of the two species was once postulated for the latter, but more recent EPR studies with **Cu4**-10.5 by Alonso *et al.* [54] and **Cu4**-12.6 and **Cu5**-12.*m* ($m=1$–6) by Ghedini *et al.* [55] have yielded results that are consistent with essentially square-planar geometry. These two groups have actually arrived at different views of the smectic phases of their complexes, and we will come back to this point later.

We now move on to look at other modifications in the *N*-aryl grouping. Complexes **M6**-*n.m* shown below could have been discussed together with the six-ring complexes such as **M3**-*n.m* viewing the common core configuration like letter "S" (rather than "Z"), but the additional phenylene groups are better regarded as special non-polar insertions into **M5**-*n.m* from the standpoint of the essentially smectogenic character. A notable feature common between the structural types of **M6** and **M3** is that the smectic property in the starting ligands tends not to be promoted upon coordination of this mode.

The phenylene groups have proven to be much more effective in promoting the smectic behavior than the ethereal oxo linkages to the alkyl groups (*ca* +10 °C in T_{AI}). This is demonstrated by series **Cu6**-*n*.12 ($n=1$–12, 18) and series **VO6**-*n*.10 ($n=4$–12, 18) with their T_{AI} values ranging in 213–295 °C [64] and 234–290 °C [65] (with falling trends) respectively. Comparisons between **Cu5**-12.8 and **Cu6**-12.12 and

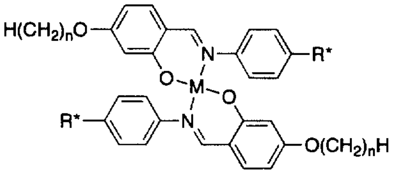


M6-*n.m*

between **VO5**-12.8 and **VO6**-12.10 show increments of 64 °C and 95 °C, respectively. These are really a substantial increase even after adjusting for the difference in *m*. Stable SmC phases have been revealed with homologues of $n \geqslant 7$ in both of these series. Complexes of other metal atoms, **Pd6**-*n*.12 ($n=1$–12, 18) [64], **Pt6**-*n*.10 ($n=$ 4–12, 18) [65], and **Ni6**-*n*.12 ($n=1$–12, 18) [66] have been reported and all of the series exhibit the same phase pattern of SmA/SmC. The presence of heavier metal atoms in the former two series causes the mesophases to appear again in very high temperature ranges and their thermal stability cannot be properly evaluated experimentally. The entire series of nickel(II) complexes has proven to be mesomorphic, unlike the complexes **Ni3**-*n.m* and **Ni4**-*n.m*, owing to a desirable effect of lifting up the mesophase areas (upper limit of 179–269 °C) while suppressing the melting temperatures (140–180 °C). A wide SmC phase area is thus clearly visible as well as the SmA area. It spans over a range $5 \leqslant n \leqslant 12$ (and $n=18$) with a maximum of 221 °C at $n=11$ and the SmA phases are completely replaced for higher homologues of $n \geqslant 10$. The apparent dominance of this SmC phase area is a result of general destabilization in the SmA and K phases, if referenced to the copper(II) congeners.

Modifications of the *N*-phenyl rings with polar groups such as F, CF_3 and CN have also been tested with the present four-ring smectogenic complexes [46], and the results show generally harmful effects of too strong an interaction. On the other hand, studies have demonstrated that the insertion of a carbonyl group at the link of a flexible alkyl chain of parent complexes **M4**-*n.m* leads to strong enhancement of the SmC phases. For example, the SmC phase area dominates the phase pattern for a series of copper(II) complexes of 4,4′-dialkanoyloxy-substituted *N*-salicylideneanilines, and the thermal stability increases by some 40 °C compared with the 4,4′-dialkoxy counterparts (**Cu4**-*n.m*) of comparable tail length [60].

A mixed alkoxy/alkanoyloxy substitution pattern has been exploited to generate ferroelectric materials by incorporating a chiral center in the *N*-aryl moiety. *n*-Butyl lactate ($-OC^{*}H(CH_3)COOC_4H_9$) was employed by the Spanish groups as a chirality source and it was linked via either ethylenecarbonyloxy (–CH=CH–COO–, designated hereafter as A*), carbonyloxy, or oxo group to the *N*-phenyl group as in **M7**-*n*.R* [67–69]. The resulting complexes of copper(II), oxovanadium(IV), and palladium(II) exhibited chiral smectic C (SmC*) phases; they proved to be thermodynamically stable only in the cases of cinnamate derivatives. SmA phases appeared on top over generally wide temperature ranges. Ferroelectric properties have been demonstrated in these SmC* phases, together with their ability as a chiral dopant [69]. Related chiral material which possesses a metastable SmC* phase was derived using *S*-(−)-β-citronellyl group as R* [70]. The other type of mixed substitution (alkanoyloxy/alkoxy) has only recently been carried out. Tian *et al.* employed chiral 2-chloro-3-methylbutyroyl groups instead of butyl groups of **Cu4**-4.*m*, and the resulting complexes **Cu4**-5*′.*m* ($m = 4$–12) exhibited SmA phases together with stable SmC* phases over only small temperature ranges with two homologues of $m = 8$ and 10 [71].



M7-*n*.*m*

An intriguing issue from the standpoint of this article is how and why the complex molecules tilt in their SmC phases. It is pretty clear from the comparisons of phase incidence that permanent dipoles play an important role, and theories are supportive of this view. Marcos and coworkers proposed that the molecular plane (the widest face of a "brick") of **M7**-10.A* lies, on the average, in the tilt plane defined by the vectors ***n*** and ***c*** (Fig. 11) in order to explain the emergence of spontaneous polarization of up to 30–90 nC cm^{-2} [69]. In this way the molecular C_2 axis (normal to the coordination plane) and the C_2 polarization axis (point group of the SmC* phase is C_2) are coincident. This proposal implies that there must be a specific asymmetry in the rotational potential that favors this particular direction of tilt (towards the edge).

Perez-Jubindo and coworkers carried out a dielectric spectroscopic study on **VO7**-10.A* [72] and interpreted the results as reflecting a cooperative flip-flop motion of the molecules around their long axes in both of its SmA and SmC* phases. A similar mode of hindered rotation was postulated by the same authors in a previous investigation with an achiral analogue **VO4**-10.5 for its I, SmA, and SmC phases in which the dielectric behavior can be more easily related to the net dipole moment associated with the V=O bond [73]. These analyses by the Spanish workers echo strongly on the notion that Alonso and coworkers have developed on the basis of their EPR experiments [44,54,74–76]. These authors seem to have a strong prefer-

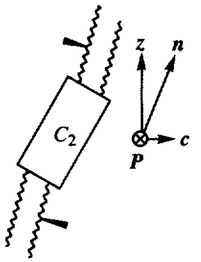


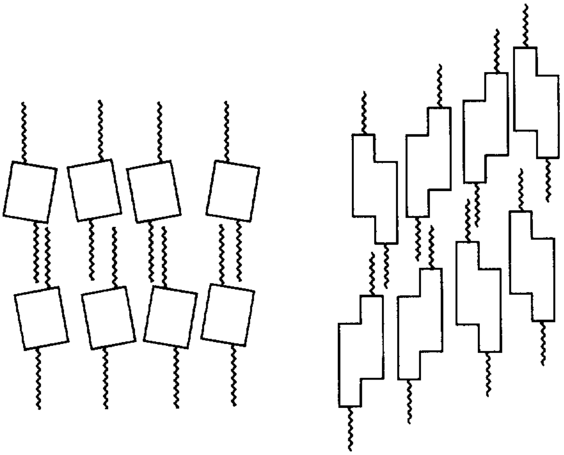
Fig. 11. A schematic representation of the molecular tilt in SmC* phases of M7-10.A* proposed by Marcos and coworkers (adapted from Ref. [69]).

ence for the exchange interactions over motional averaging of magnetic interaction tensors in interpreting the spectral shapes observed in condensed smectic phases. Apart from the cases of oxovanadium(IV) complexes (**VO1**-10.5 and **VO2**-10.5 [74]) and of copper(II) complexes in their N phases (**Cu1**-10.5 and **Cu2**-10.5 [76]), the loss of apparent hyperfine splitting is always thought to indicate strong exchange interactions. For instance, an EPR spectrum of solid **Cu4**-10.5 with no hyperfine structure ($g_x=2.04$, $g_y=2.08$, $g_z=2.21$) was interpreted to reflect the exchange averaging of the g-tensor components ($g_x=2.04$, $g_y=2.05$, $g_z=2.24$, $A_{\parallel}=485$ MHz, frozen solution) [54]. The spectrum recorded for the smectic phases (both SmA and SmC) displaying a nearly isotropic signal at $g_0=2.10$ was used to argue that a spectrum under motional averaging alone would show effective g-factors of $g_{\perp}\approx 2.14$ and $g_{\parallel}\approx 2.08$. It was thereby deduced that the exchange interaction was significant even in the smectic phases leading to the collapse of hyperfine structure. This, in turn, led the authors to believe that there existed some kind of short-range order within the smectic layers to ascertain the exchange pathway. The EPR spectral changes with temperature were also analyzed for **VO4**-10.5 and it was concluded that "in the smectic phases the motional mode around the long axis is a restricted libration of small angular amplitude" [1].

Ghedini *et al.* [55], on the other hand, reported the EPR spectra and parameters for related complexes **Cu4**-12.6 and **Cu5**-12.*m* ($m=1$–4, 6, 8) and commonly rhombic spectra ($g_1=2.13$–2.15, $g_2=2.10$–2.12, $g_3=2.05$–2.06), recorded in their SmA phases and simulated using Lorenzian line shapes, were characterized by the greater linewidths and smaller $|g_1-g_2|$ with respect to the room-temperature spectra. These authors deduced that "the formation of these SmA phases is accompanied by a disordering in the structure of the compounds with an increase in the misalignment in the principal directions of the molecular g-tensor." Thus, two different views have been derived from different analyses of the spectra: namely, the hyperfine splitting is either averaged to zero due to the exchange interactions or just unresolved. Unfortunately, it is difficult to separate the exchange and the motional effects for magnetically concentrated samples of copper(II) complexes [75,76]. It would be desirable to devise experiments to extract information on the spatial decorrelation of principal axes of both g and A tensors that signify motions inherent to the liquid crystal.

The EPR techniques were truly powerful in an early demonstration of the facile orientation by the magnetic field of nematic samples of oxovanadium(IV) complexes such as **VO1**-10.5 [42]. Smectic materials are also alignable by the magnetic field and a number of copper(II) mesogens have been subjected to the study of their anisotropic magnetic susceptibilities and its relation to the macroscopic alignment. A recent survey of 16 copper(II) and eight oxovanadium(IV) complexes of various salicylaldimine derivatives [77] summarizes the behavior as follows. If the number of phenyl rings in the molecule is greater than four, then the positive diamagnetic anisotropy exceeds that of the negative paramagnetic contribution from the copper(II) center, and the molecular long axis (and the director consequently) tends to align parallel to the external magnetic field. Otherwise the long axis of the copper(II) complex tends to orient perpendicular to the field. The paramagnetic anisotropy for oxovanadium(IV) complexes has been calculated to be invariably positive, and this agrees well with the observed parallel alignment. Noting further that the above-mentioned 5-isomer **Cu1**′-10.1 can be aligned parallel to the magnetic field in its SmC phase [33] in spite of having only four phenyl rings, Alonso and Martinez have pointed out that the "additional ordering of the short molecular axes" must be considered [78]. The importance of taking the *molecular* biaxiality, to be more precise, into account has been stressed recently by Ovchinnikov and Prosvirin [79].

X-ray diffraction studies with magnetically oriented, monodomain samples of nematic and smectic materials [33,44,80,81] have complemented the above arguments of magnetic properties. In addition, some unusual features have been disclosed for the one-dimensional lattice structure in metal–salicylaldimine smectics and their precursor state (skewed cybotactic groups or the smectic C fluctuations have been confirmed by this method in the nematics). First of all, it has often been found that the apparent molecular length l_X, determined from the low-angle diffraction spots by the relation $l = d/\cos\alpha$ (d is the lattice constant), is more comparable with (and in fact even smaller than) the length of a ligand l_L rather than of the whole complex molecule. The terminal chains span longer than the lateral chains in the compounds showing this behavior: **M1**-10.10 (M = Cu, Ni, VO) in their N phases [33]; **Cu2**-4.1, **Cu2**-6.1, and **Cu2**-6.4′ (butyl instead of butoxy) in their N phases [81]; **M2**′-10.*m* (M = Cu, VO; $m = 2$, 5, 9; methyleneoxy instead of carbonyloxy linkages) in their SmA and SmC phases [44]; **Cu5**-12.4 and **Cu5**-7.4 in their SmA phases [80]. A structural model involving deep interdigitation of the molecules, as shown below, is consistent with the results. We also carried out a structural investigation into a wide series of smectogenic complexes **Cu4**-*n*.2 ($n = 3$–18) [50]. The layer distance data collected at reduced temperatures of $T/T_{AI} = 0.96$–0.99 were fit reasonably to a linear equation $d/\mathrm{nm} = 1.624 + 0.127n$ in accord with a complete interpenetration. The slope corresponds to the increment by one methylene group in the all-trans aliphatic chain, and this holds for the entire series in this case.



Reports also exist for exceptional cases of *N*-methyl derivatives **Cu1**-10.1 and **Cu1′**-10.1, in which the structures of their smectic C fluctuation and SmC phase respectively can be explained with no need for the interdigitation model. "Partial" cases have also been found in **M1**-10.5 and **M2**-10.1 (**M**=Cu, Ni, VO), where the values of l_X are larger than l_L (in fully extended conformation) [33]. These homologues with clipped lateral alkyl groups do not require a full interdigitation. Good mutual packing of the aliphatic tail portions is a key to the formation of smectic phases.

The second feature of interest from a structural viewpoint is that a so-called side-by-side correlation has been recognized. A mid-angle diffuse scattering was detected in the direction perpendicular to the director in the SmA phase of **Cu5**-12.4 [80]. The distance of 0.85 nm corresponding to the intensity maximum fits to a pair configuration in which molecular edges are in contact, if the molecular section of a complex in the layer is approximated as a rectangle of 0.4×0.9 nm^2. It is not clear how to rationalize such nematic ordering (even over a short range) within the smectic layer, but another mode with face-to-face correlations that one might expect based on stacking interactions has been denied. Therefore, it must somehow be a consequence of hindered rotations. A possibly related phenomenon has been reported for **Ni2**-10.1 cited above [33]. The X-ray diffraction pattern recorded in its N phase is more consistent with smectic A fluctuations (rather than C as in other metal complexes) and, in addition, a diffuse scattering corresponding to the distance of 1.15 nm has been observed. This could be due to a local ordering similar to the above case, considering the possibly distorted structure of this nickel(II) complex as a source of the increased size of the correlated configuration. Since such correlations have so far been detected only in orthogonal smectics of metal–salicylaldimine complexes, our attention is directed again to the related role of alkyl chain packing. Smectic polymorphism has been analyzed in our laboratory for a wide series of achiral complexes with alkoxy/alkanoyloxy substitution pattern, and thus related to the structural type of **Cu7**. It has been demonstrated that the tilted SmC phases in the complexes are not as stable (relative to the SmA phases) as in the corresponding organic ligands [82]. A decreased incidence of SmC phases among the copper(II) complexes, especially with short terminal tails, seems to have some relevance to the need for the orthogonal chain packing. However, it cannot be factored out from the influence of permanent dipole moments, which could be quite different between the ligands and the centrosymmetric complexes.

Interdigitated structures of metallomesogenic compounds have been found in their crystalline states, where the projection-hollow principle is predominant. Explicitly layered organizations revealed by the single crystal work were used by Polishchuk and Timofeeva to calculate the intermolecular pairwise interaction energies with special interest in the intra- *vs* inter-layer energy ratio [8]. The values calculated for homologous members **Cu4**-7.1 and **Pd4**-7.1 are about 5 and 3.5 respectively, taking only the dispersion components. Here the interlayer contacts are between the alkyl chains alone and it can be easily imagined that partial fusion of these chains would allow almost free sliding of layers, according to the authors. The mode of parallel packing of terminal parts of all-trans dodecyl chains is illustrated well in the crystal structure of **Cu5**-12.3 [83]. This material undergoes a solid–solid transformation prior to the formation of its SmA phase and it is likely that the high-temperature phase involves an extensive disordering in the chains. These crystal structures are in all cases "prosmectic C" type (rather than A) with variable "tilt" angles. Therefore, the information we are looking for is buried in the melting process at the K/SmA interface in these cases.

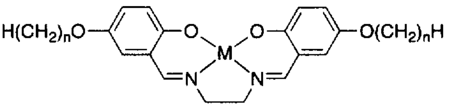
In summary, the smectic phases of metal–salicylideneaniline complexes are characterized by the unconventional molecular shape. The influence of molecular biaxiality has been hinted upon, although macroscopic biaxial ordering in the SmA phases has not been confirmed. With the core length/breadth ratio decreased, the relative importance of the factor of aliphatic chain packing seems to have increased. As a consequence, the molecular rotational dynamics must be in a strongly hindered and biased state. The question as to what kinds of interaction determine the molecular tilt (its direction and size) in the SmC phases of metallomesogens remains unresolved. The work has so far been centered around copper(II) complexes; synthesis and NMR investigations of diamagnetic counterparts having manageable melting and clearing temperatures would be fruitful.

4.3. Columnar phases

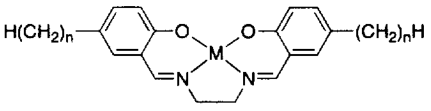
H_2salen (*N*,*N*′-disalicylideneethylenediamine) is perhaps the best known salicylaldimine ligand. Complexes of [M(salen)] type, however, have not been utilized as much as the previous bis-chelate complexes in the derivatization for mesomorphous materials. While there exists a broad background chemistry established for the [M(salen)] complexes and some of the aspects such as catalysis would be further enriched if conducted in the mesophases, it has been a more challenging task to control strong intermolecular interactions involving the rather exposed metal centers.

In fact, one of the characteristic structural motifs found in this family is the formation of centrosymmetric, either face-to-face stacked [84] or axially interacting, offset [85] dimers. With such units having been recognized in the crystalline state of the framework complex, a question naturally asked is what kinds of species would constitute liquid crystals when appropriate modifications have been performed. It should be noted that the present *cis*-N_2O_2 coordination would allow a net dipole moment to reside at the molecular center, whereas the polarization of coordinate bonds in the trans bis-chelates previously considered is fully cancelled (or nearly so). Therefore, it will become a critical problem as to whether the dimerization persists or not in the mesophases when we consider the construction of polar liquid crystal materials. If the dimeric unit splits into monomers, then we will have a new opportunity to study the effect of molecular symmetry; [M(salen)] derivatives will have a $C_2(x)$ axis within the chelate plane unlike the bis-chelate complex in which the $C_2(y)$ axis is perpendicular to the plane. Since restricted rotations about the z axis are suspected for certain mesophases based on the discussion in Section 4.1 and Section 4.2, the mesomorphic property may be affected by the switching of the molecular symmetry axis.

The reported examples of 5,5′-dialkoxy and -dialkyl derivatives, which are in fact smectogenic, are cited first for the purpose of illustrating a straightforward modification to the calamitics and contrasting it to the derivatization for columnar liquid crystals. Selected homologues of such alkylated derivatives **M8-*n*** and **M9-*n*** shown below are listed in Table 1 and their phase transition temperatures are quoted.



M8-*n*



M9-*n*

The liquid crystalline phases emerge at quite high temperature ranges in these complexes and, when they do, they are invariably SmA phases. The thermal stability of these phases in copper(II) complexes appears to be lower than in nickel(II) complexes by 27–28 °C, which is reminiscent of the comparison between the N phases of another group of *N*-alkyl derivatives **M1-*n.m*** (M = Ni, Cu). Compared with cobalt(II) species, the temperature ranges for the copper(II) complexes are substantially narrowed by the rise in their melting temperatures. The 4,4′-difluoro substitution has proven to be detrimental to the mesophases against the expectation for reduced melting points as in the organics, but this can be taken as support for the calamitic character of these mesophases.

Crystal structures of **M8-*n*** and **M9-*n*** have been determined only for nickel(II) complexes. In the case of **Ni9-6**, the molecules form a centrosymmetric face-to-face dimer as in the framework complex [Ni(salen)], but almost uniformly stacked along

Table 1
Mesomorphic phase transition temperatures (°C) for selected homologues of complexes **M8-*n*** and **M9-*n***

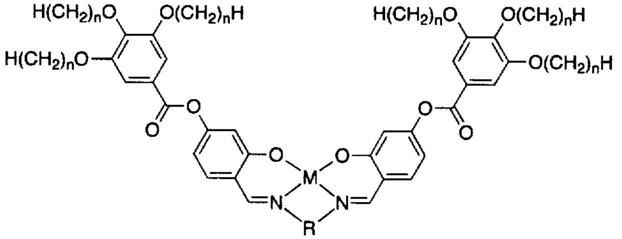
M	*n*	R[a]	Z[b]	K_3		K_2		K_1[c]		SmA		I	
VO	8	H	O			·	62	·	179	·	198	·	[86,87][d]
VO	8	F	O					·	198			·	[88]
Co	8	H	—	·	122			·	215	·	283	·	[89]
Co[e]	8	H	O			·	137	·	173	·	278	·	[89]
Co[f]	8	H	O	·	68	·	125	·	173	·	277	·	[89]
Ni	6	H	—			·	126	SmE	226	·	258	·	[90]
Ni	6	H	—	·	84	S_2	118	S_1	245	·	310	·	[91]
Ni	6	H	O					S_1	214	·	299	·	[91]
Ni	8	H	—			·	86	S_1	230	·	308	·	[91]
Ni	8	H	O			·	61	S_1	186	·	300	·	[91]
Ni	8	F	O					·	250	(·	246)	·	[88]
Cu	8	H	—					S_1	235	·	280	·	[91]
Cu	8	H	O					·	248	·	273	·	[91]
Cu	8	F	O					·	255			·	[88]

[a] Substituents in 4,4′-positions of the disalicylidene moiety.
[b] Z = O and none for complexes **M8-*n*** and **M9-*n***, respectively.
[c] Crystal smectic phases are indicated in this column where identified.
[d] Data on cooling.
[e] Polymorph inactive to dioxygen, as prepared.
[f] Polymorph active to dioxygen, obtained by recrystallization.

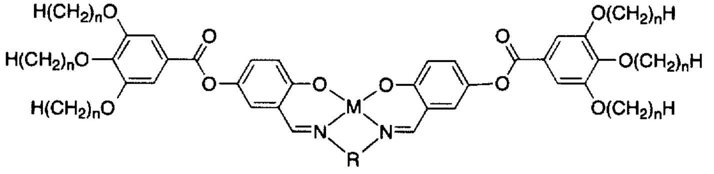
the [001] direction in a triclinic crystal of $P\bar{1}$ space group [88]. Relatively short Ni···Ni distances of alternately 3.400 Å and 3.406 Å have been found ($c = 6.65$ Å). The shortest distances from the nickel atom to the donor nitrogen atoms in neighboring molecules occur at 3.45 Å, and thus the molecules are slightly offset laterally. It appears from the unit-cell dimensions that these ribbons are organized into a stratum motif of prosmectic C arrangement ($\gamma = 71.4°$). The hexyl chains are assigned with large thermal vibrational factors and bent away from the plane defined by the chelate core. It appears, therefore, as if the structure was governed by the parallel core packing and the alkyl groups managed to fill the rest of space. The alkoxy counterpart of this complex crystallizes as monohydrate, and the crystal structure of [**Ni8**-6]·H_2O contains better-defined dimeric units which are packed in a double herringbone fashion [91]. However, the centrosymmetric dimer involves a much greater displacement (Ni···Ni = 6.87 Å) and the shortest intermolecular contacts of the nickel atoms are now 3.75 Å and 3.97 Å to hexyloxy oxygen atoms and 3.81 Å to a ring 5-carbon atom of neighboring dimers [88]. Water molecules are located within hydrogen bonding distances from ligating oxygen atoms. The hexyloxy tails are extended in the all-trans conformation and lie approximately in the chelate plane and all point roughly along the same direction in the crystal.

It may be learned from these examples that the centrosymmetric dimers would still occur after the alkylating substitutions, but its discreteness can be varied greatly by other factors. Both of these crystals eventually transform into the SmA phases via different phase transition events. An X-ray investigation into a so-called SmE and the SmA phases of **Ni9**-12 was carried out by Ohta *et al.* They concluded that the dimeric units split at the SmE→SmA transition [90]. While this is a likely event, there are some inconsistencies. The dimeric unit postulated for the low-temperature ordered smectic phase was thought to be, and called, "slipped dimers" in order to explain the observed decrease in layer distance by about 5 Å upon splitting, whereas the coauthors had previously denied such a mode of aggregation in favor of the face-to-face version from their own study in the solution phase [92]. Moreover, the transition temperatures reported at the same time for its homologous member **Ni9**-6 were much lower than the literature data [91] (see Table 1). Paschke *et al.* [91], on the other hand, noticed that the copper(II) complexes decomposed rapidly after entering the SmA phase, and explained the generally lowered values of T_{AI} for them (relative to nickel(II) and cobalt(II) congeners) invoking the necessity of the axial interaction for the stability of copper(II) species. It is thought here that the molecules are forced to lie parallel in layers and the stabilization of the copper(II) chelate by the axial interactions involving neighboring oxygen atoms is no longer possible. Thus, it seems to be acceptable, albeit through different reasoning, that the constituent molecules are monomeric as far as the SmA phases are concerned.

In marked contrast to these relatively conservative approaches is a rather drastic modification of the ligand made by Serrette and Swager [93] to produce **M10**-R-*n* and **M11**-R-*n* (M = VO; $n = 14$) shown below. Here the alkylene bridge R is chosen from 1,2-ethylene (en), 1,3-propylene (tn), and 2,2-dimethyl-1,3-propylene (dmtn) groups. If 4-alkoxybenzoyloxy substituents were employed, more straightforward counterparts to complexes **M1**-*n*.1 and **M1′**-*n*.1 would have been derived. They would also be regarded as useful analogues of **M8**-*n* with *p*-phenylenecarbonyloxy groups inserted. Unfortunately, however, the presence of only two terminal chains is insufficient for any mesophases to emerge [94]. After all, only columnar mesomorphism is observed with new complexes **VO10**-R-14 and **VO11**-R-14. The behavior must be due partly to the presence of densely incorporated long alkyl chains.



M10-R-*n*



M11-R-*n*

Swager and coworkers were the first to try to exploit the "dative bonding" between oxovanadium(IV) groups forming a polymeric V=O···V=O··· chain and an overall columnar superstructure. In fact, tuning of such interactions was attempted with simpler derivatives **VO8**-*n* (*n*=4–8, 10, 12) synthesized first [86,87]. The highest three homologues turned out to possess SmA phases. Expansion of the salen chelates to saltn analogues led to a stronger chain structure and the materials did not melt easily. 2,2-Dimethylation was effective in reducing the melting temperatures, but the resulting complexes still exhibited only crystal smectic phases. The V=O stretching vibration in the IR spectrum is diagnostic of the dative bonding, and the variable-temperature spectroscopy revealed [93] that both of the new salen derivatives **VO10**-en-14 and **VO11**-en-14 were monomeric throughout the phase sequence of $I \rightarrow D_{hd}$ ($\upsilon_{VO}=992\ cm^{-1}$). On the other hand, **VO10**-R-14 (R=tn, dmtn) and **VO11**-tn-14 showed evidence for the interaction active in the columnar phases ($\upsilon_{VO}=854$–$911\ cm^{-1}$). These complexes are highly polymorphous and three different D_{hd} phases have been assigned for the former two 4,4′-isomers. It is difficult to analyze the thermodynamic parameters for systems of this complexity, but it seems that the contribution of dative bonding is reflected in the generally increased thermal stability of the highest-temperature D_{hd} phases of both **VO10**-tn-14 and **VO11**-tn-14 (175 °C and 170 °C for $D_{hd1} \rightarrow I$ transitions) relative to the monomeric salen analogues (150 °C and 156 °C). Similarities in the hexagonal lattice constants between the 4,4′- and 5,5′-isomers (4.47 nm and 4.65 nm for R=en, and 4.46 nm and 4.32 nm for R = tn) have been interpreted to indicate "correlated columnar superstructures", which in both cases have circular intersections on the time average.

However, it is not easy to reconcile the facts that the diffraction data are consistent with liquid-like columns and that the IR evidence indicates $V{=}O\cdots V{=}O\cdots$ chains which are suggested to be polymeric. The systems with specific bonding interactions may be better regarded as a result of coupling of liquid crystal ordering to self-assembly [95]. The intrinsic property of such self-assembling systems is a broad size distribution of the particles and its variability with conditions. It may be worthwhile to evaluate the results obtained with the above columnar materials in this light. The controlled alignment of the $V{=}O$ bonds bears dual tasks in the authors' scheme: formation of the columnar phase and the ferroelectric dipolar ordering. However, a recent computer simulation study of 10^3 discotic particles with a central axial dipole has revealed that aligned dipolar domains are formed in a column at low temperatures, but no fully polarized columns nor overall phase ferroelectricity is found [96].

There is a wide spectrum of novel phases between these columnar liquid crystals supported by the axial bonding interactions and the preceding SmA phases with diminished dimerizing interactions. Half-disc-shaped complexes similar to **M10**-R-*n*, but of plain metal atoms and perhaps fewer aliphatic chains, might be a good candidate for biaxial SmA materials. Ferroelectricity in smectic phases of achiral, "banana-shaped" molecules is of much current interest [97]. Good use can be made of the permanent dipole moments also associated with the coordinate bonds, and the bulk polarization may develop along the possible ordering direction for the $C_2(x)$ axis of each molecule within a layer. We have investigated some nickel(II) and copper(II) analogues of **M10**-R-*n* and **M11**-R-*n* and obtained rather intriguing results, possibly arising from the intermediacy between the calamitic and the columnar characters [98].

5. Concluding remarks

Mesomorphic properties of metal–salicylaldimine complexes have become quite diverse over the decade, but hopefully this article shows that a reductionistic approach still works. The shape anisotropy provides the necessary entropy drive, and the attractive interactions can also be accounted for basically in a similar manner to the organic liquid crystals. This is a natural consequence of a smaller density of the metal within the molecule and its structurally confined nature for the present examples. The bonding interactions among, or self-assembly of, coordinatively unsaturated species are definitely unique to metallomesogens. Their relevance or influence has been frequently suggested in this article.

Metallomesophase materials will be useful as a soft assembly of metal complexes in which they have acquired new functions in exchange by losing part of their solid state order: facilitated responses to external triggers, increased processability to a large size domain, and stability to and self-annealing of structural defects, to name a few. A key to the understanding and utilization of the materials is a knowledge of the exact dynamical state with molecular details. The strongly correlated rotational state suggested for the metal–salicylaldimine smectics is a promising function of transducing external stimuli, maybe slowly but efficiently. More effort should be expended for careful syntheses of pure materials and accurate evaluations of the results, but exploration into unknown systems must also continue in order to maintain the impetus. This article will hopefully give a chance for fellow coordination chemists to take a fresh look at their favorite compounds.

Acknowledgements

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